source temperature below 100°. Samples were introduced *via* the heated inlet system at a temperature below 80°. Unimolecular metastable transitions in the second drift region were observed at a nominal 8 kV. Collision-induced metastable transitions were observed using helium at a pressure of 7×10^{-6} τ. The first drift region transitions were obtained using the metastable refocussing technique.[7]

Unlabeled compounds were either available commercially or synthesized by unexceptional methods.

Isotopically labeled compounds were prepared as outlined in Scheme III.

Acknowledgment. N. A. U. (on leave from Istituto di Chimica Organica–Gruppo Sintesi Chimiche del CNR, Universita di Messina, Italy) wishes to thank his Institute for a grant. We wish to thank the Science Research Council for financial support of this work.

Kinetic Applications of Electron Paramagnetic Resonance Spectroscopy. VIII. Tetraalkoxyphosphoranyl Radicals[1]

G. B. Watts,[2] D. Griller, and K. U. Ingold*

Contribution from the Division of Chemistry,
National Research Council of Canada, and the Christopher Ingold Laboratories,
University College London, London, England.
Received April 28, 1972

Abstract: The reactions of the phosphoranyl radicals formed by the addition of *tert*-butoxy radicals to trimethyl, triethyl, triisopropyl, and tri-*tert*-butyl phosphite have been examined by epr spectroscopy. At temperatures below *ca.* −115° the $t\text{-BuO}\dot{P}(OMe)_3$ and $t\text{-BuO}\dot{P}(OEt)_3$ decay with second-order kinetics. At higher temperatures all four radicals decay with first-order kinetics to yield phosphate and a *tert*-butyl radical. The rates of this β-scission reaction increase by about an order of magnitude at −60° along the series from $t\text{-BuO}\dot{P}(OMe)_3$ to to $(t\text{-BuO})_4\dot{P}$. Arrhenius parameters for β-scission have been determined by kinetic epr spectroscopy and by a competitive procedure. The latter method has shown that *tert*-butyl radicals react with phosphoranyl radicals with rate constants that are approximately the geometric mean of the rate constants for the bimolecular self-reactions of the *tert*-butyl and phosphoranyl radicals. The mechanism of β-scission is discussed.

The growing importance of free radical reactions in organophosphorus chemistry is well documented.[3] The presence of unoccupied low energy d orbitals makes valence shell expansion of tervalent phosphorus compounds possible. Such compounds can therefore react with free radicals to increase their coordination number to four and yield a *phosphoranyl radical*[4–6] with nine valence electrons.

$$Y\cdot + PX_3 \longrightarrow Y\dot{P}X_3$$

Tetraalkoxyphosphoranyl radicals have been proposed as intermediates in the oxidation of trialkyl phosphites by *tert*-alkoxy radicals.[4,6]

$$R'O\cdot + (RO)_3P \longrightarrow R'O\dot{P}(OR)_3 \longrightarrow R'\cdot + OP(OR)_3$$

Initial attempts to observe such phosphoranyl radicals directly by the photolysis of di-*tert*-butyl peroxide in the presence of trialkyl phosphites in the cavity of an electron paramagnetic resonance (epr) spectrometer were unsuccessful, only the spectrum of the *tert*-butyl radical being observed.[7–9] However, more recent work has shown that this failure was due to an insufficient sweep of the magnetic field in these experiments.[11–14] Trialkoxy(*tert*-butoxy)phosphoranyl radicals and trialkoxy(ethoxy)phosphoranyl radicals[15] have now been detected from a wide variety of trialkyl phosphites. The epr spectra of these radicals show a large doublet splitting from phosphorus (∼900 G) with no further fine structure.[11–15] Phosphoranyl radicals are believed to have a slightly distorted trigonal-bipyramidal structure, with the orbital of the unpaired electron occupying a position in the equatorial plane.[12,13,16]

Bentrude and coworkers[17–19] have studied the stereochemistry of the overall oxidation of trialkyl phosphites

---

(1) Issued as N.R.C.C. No. 12929. Part VII; J. L. Brokenshire, J. R. Roberts, and K. U. Ingold, *J. Amer. Chem. Soc.*, **94**, 7040 (1972).

(2) N.R.C.C. Fellow, 1970–1971.

(3) See, *e.g.*, J. I. G. Cadogan, *Quart. Rev., Chem. Soc.*, **16**, 226 (1962); *Advan. Free-Radical Chem.*, **2**, 203 (1968); R. F. Hudson, "Structure and Mechanism in Organophosphorus Chemistry," Academic Press, London, 1965, Chapter 9; C. Walling and M. S. Pearson, *Top. Phosphorus Chem.*, **3**, 1 (1966); A. J. Kirby and S. G. Warren, "The Organic Chemistry of Phosphorus," Elsevier, Amsterdam, 1967; K. U. Ingold and B. P. Roberts, "Free Radical Substitution Reactions," Wiley-Interscience, New York, N. Y., 1971, Chapter 6; W. G. Bentrude, *Annu. Rev. Phys. Chem.*, **18**, 283 (1967).

(4) C. Walling and R. Rabinowitz, *J. Amer. Chem. Soc.*, **79**, 5326 (1957); **81**, 1243 (1959).

(5) F. Ramirez and N. McKelvie, *ibid.*, **79**, 5829 (1957).

(6) C. Walling and M. S. Pearson, *ibid.*, **86**, 2262 (1964).

(7) J. K. Kochi and P. J. Krusic, *ibid.*, **91**, 3944 (1969).

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

(9) However, a phosphoranyl radical was detected with trimethylphosphine.[7,10]

(10) J. K. Kochi and P. J. Krusic, *Chem. Soc. Spec. Publ.*, No. 24, 147 (1970).

(11) A. G. Davies, D. Griller, and B. P. Roberts, *Angew. Chem.*, **10**, 738 (1971).

(12) A. G. Davies, D. Griller, and B. P. Roberts, *J. Chem. Soc., Perkin Trans. 2*, 993 (1972).

(13) P. J. Krusic, W. Mahler, and J. K. Kochi, *J. Amer. Chem. Soc.*, **94**, 6033 (1972).

(14) G. B. Watts and K. U. Ingold, *ibid.*, **94**, 2528 (1972).

(15) A. G. Davies, D. Griller, and B. P. Roberts, *J. Chem. Soc., Perkin Trans. 2*, submitted for publication.

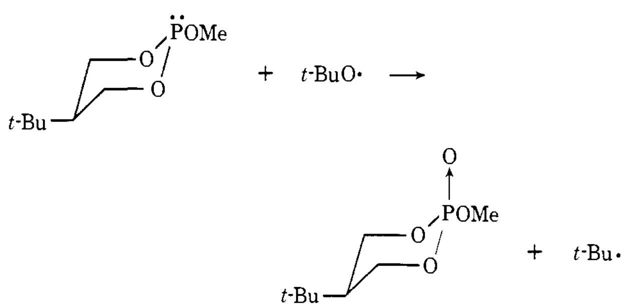
(16) J. Higuchi, *J. Chem. Phys.*, **50**, 1001 (1969); R. W. Fessenden and R. H. Schuler, *ibid.*, **45**, 1845 (1966).

(17) W. G. Bentrude, J. H. Hargis, and P. E. Rusek, Jr., *Chem. Commun.*, 296 (1969).

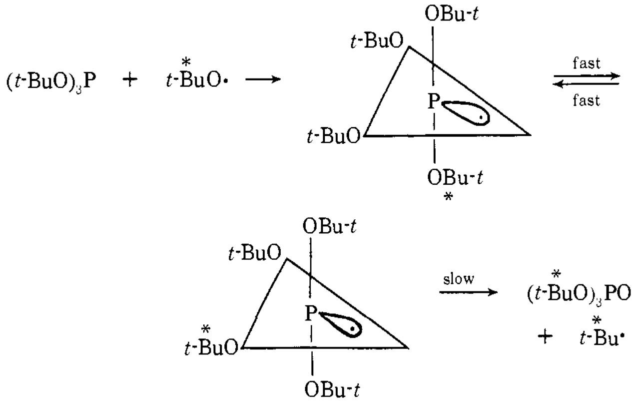
(18) W. G. Bentrude and R. A. Wielesek, *J. Amer. Chem. Soc.*, **91**, 2406 (1969).

(19) W. G. Bentrude and T. B. Min, *ibid.*, **94**, 1025 (1972).

to phosphates by alkoxy radicals. It might be expected that the stereochemical outcome depends on the configurational stability and lifetime of the phosphoranyl radical which is determined by the nature of the substituents around the phosphorus. The transfer of oxygen from *tert*-butoxy radicals (and of sulfur from *n*-butylthiyl radicals) to give oxide (or sulfide) occurs, as would be expected, stereospecifically and with retention of configuration at phosphorus in the geometrically isomeric (cis–trans) pair of 2-methoxy-5-*tert*-butyl-1,3,2-dioxaphosphorinans,[17,20] *e.g.*



The thermolysis of ^{14}C-labeled di-*tert*-butyl hyponitrite in the presence of tri-*tert*-butyl phosphite in benzene at 65° produced tri-*tert*-butyl phosphate in almost quantitative yield and approximately 75% of the phosphate was ^{14}C-labeled.[18] This result was interpreted in terms of the essentially irreversible formation of a phosphoranyl radical with statistical scrambling of the label. If an unsymmetrical intermediate is formed initially it must have a lifetime sufficient to allow equilibration of configurationally nonequivalent groups by some process such as pseudorotation, assuming that the *tert*-butoxy groups are not reactionally equivalent.



More recently,[19] it has been found that in the reaction of benzyloxy radicals with benzyl diethyl phosphite (one of the benzyl groups being chemically labeled with a *p*-methyl group) the predominant phosphate (1.2:1.0) is that which results from transfer of oxygen from the incoming alkoxy radical. This result is not necessarily in conflict with the tri-*tert*-butyl phosphite experiments since the difference in reactivity between incoming and attached alkoxys predicts a deviation from statistical ^{14}C distribution within the error limits of the counting technique. However, it is also possible that the stereoselectivity observed in the later experiments is related to the expected shorter lifetime of the dibenzyloxydiethoxyphosphoranyl compared with tetra-*tert*-butoxyphosphoranyl which results from the greater stability of a benzyl compared with a *tert*-butyl radical.

There have been relatively few kinetic studies on phosphoranyl radicals. Competitive methods have been used to determine the rate of formation of t-BuO$\dot{\text{P}}$(OEt)$_3$ from *tert*-butoxy and triethyl phosphite in cyclohexane[6] and in cyclopentane.[11,12] The rate of decomposition of this radical to *tert*-butyl and triethyl phosphate has also been studied in cyclopentane by a competitive procedure.[11,12] The present paper reports a systematic investigation, in a variety of hydrocarbon solvents, of the unimolecular decomposition and bimolecular self-reactions of t-BuO$\dot{\text{P}}$(OR)$_3$ radicals derived from trimethyl, triethyl, triisopropyl, and tri-*tert*-butyl phosphites. This series was chosen to see if steric effects were of importance in phosphoranyl radical reactions. Some experiments on a dioxaphosphorinan and on a benzyloxy radical–phosphite reaction are also reported.

Experimental Section

Trimethyl, triethyl, and triisopropyl phosphites were commercial materials which were purified before use. Tri-*tert*-butyl phosphite was prepared by the method of Mark and Van Wazer,[21] and 2-methoxy-1,3,2-dioxaphosphorinan by the method of Lucas, Mitchell, and Scully.[22] Solvents were reagent grade liquids and high purity gases that were deoxygenated before use. Di-*tert*-butyl peroxide was commercial material that was freed from hydroperoxide by passage through alumina.

The general experimental procedures for radical generation and for measurement of radical concentrations have been described in previous papers in this series.[1] The phosphoranyl radicals were generated in the cavity of the epr spectrometer by photolysis of deoxygenated solutions of the phosphites containing di-*tert*-butyl peroxide.

$$t\text{-BuOOBu-}t \xrightarrow{h\nu} 2\ t\text{-BuO}\cdot$$

$$t\text{-BuO}\cdot + (\text{RO})_3\text{P} \longrightarrow t\text{-BuO}\dot{\text{P}}(\text{OR})_3$$

The g values and $a(^{31}\text{P})$ values for most of the phosphoranyl radicals studied in this work have already been reported in cyclopentane.[12] The values found in cyclopropane at −70° are listed in Table I.

Table I. Epr Parameters for Some Phosphoranyl Radicals in Cyclopropane at −70°

Phosphoranyl	$a(^{31}\text{P})$,[a] G	g[a]
t-BuO$\dot{\text{P}}$(OMe)$_3$	887	2.003
t-BuO$\dot{\text{P}}$(OEt)$_3$	889	2.004
t-BuO$\dot{\text{P}}$(OPr-i)$_3$	900	2.003
(t-BuO)$_4\dot{\text{P}}$	918	2.004
t-BuO(MeO)$\dot{\text{P}}$O(CH$_2$)$_3$O	945	2.003

[a] These parameters were determined using the measured line positions and the microwave frequency in conjunction with the Breit–Rabi formula. P. W. Atkins and M. C. R. Symons, "The Structure of Inorganic Radicals," Elsevier, Amsterdam, 1967, p 238.

The phosphoranyl radicals decayed both by first-order and by second-order processes, the former predominating at higher temperatures. The rates of both processes were measured directly[1] in propane (chosen because of its low freezing point, −190°) as solvent. The activation parameters for the first-order decay of triethoxy(*tert*-butoxy)phosphoranyl did not agree very well with those previously reported for the decay of this radical in cyclopentane using a competitive method.[11,12] For this reason measure-

---

(20) Stereospecific oxygen transfer with retention of configuration also occurs with optically active methylphenyl-*n*-propylphosphine.[17]

(21) V. Mark and J. A. Van Wazer, *J. Org. Chem.*, 29, 1006 (1964).

(22) H. J. Lucas, F. W. Mitchell, and C. N. Scully, *J. Amer. Chem. Soc.*, 72, 5491 (1950).

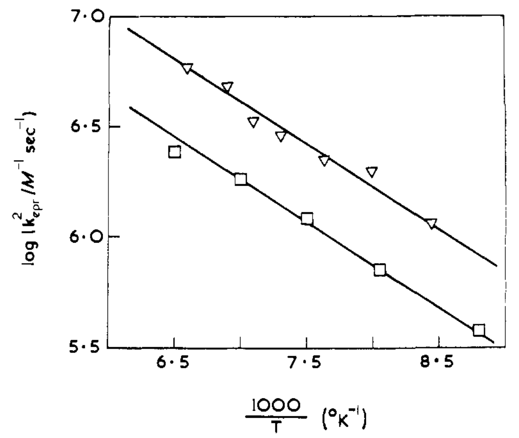


Figure 1. Log (k^2_{epr}/M^{-1} sec^{-1}) as a function of temperature for t-BuO$\dot{P}$(OMe)$_3$ (▽); and t-BuO$\dot{P}$(OEt)$_3$ (□).

ments by the competitive method were made in propane and also in a number of other hydrocarbon solvents. The estimated rate constants were generally in good agreement with one another and with the directly measured values. However, the activation parameters showed quite wide variations, apparently because they are so dependent on small changes in the least accurate rate constants obtained at the highest and lowest temperatures.

Results

Decay Measurements on Phosphoranyl Radicals. The radicals were generated by photolysis of peroxide–phosphite–propane mixtures (1:1:15 by volume). The phosphoranyl radicals decayed with first-order kinetics at higher temperatures and with second-order or mixed first- and second-order kinetics at lower temperatures–(see Table II).

Table II. Temperature Ranges (°K) for First-, Mixed-, and Second-Order Decays of Tetraalkoxyphosphoranyl Radicals in Propane

Phosphoranyl	Decay Order[a] First	Mixed[b]	Second[b]
t-BuO$\dot{P}$(OMe)$_3$	230–185°	180–165°	160–120°
t-BuO$\dot{P}$(OEt)$_3$	225–175°	170–160°	155–115°
t-BuO$\dot{P}$(OPr-i)$_3$	210–160°	155–120°	
(t-BuO)$_4\dot{P}$	205–150°	145–120°	

[a] In these experiments the upper temperature limit was determined by the phosphoranyl concentration becoming too low for the direct measurement of decay rates. The lower temperature limit was determined by the solubility of the reagents. [b] Under full light intensity the steady-state phosphoranyl radical concentrations were ~2 × 10^{-6} M.

Bimolecular rate constants, k^2_{epr}, for the second-order decay of trimethoxy(*tert*-butoxy)- and triethoxy(*tert*-butoxy)phosphoranyl radicals were measured over the temperature ranges indicated in Table II, and over ranges in initial phosphoranyl concentration from 2 × 10^{-7} to 2 × 10^{-6} M.

$$2t\text{-BuO}\dot{P}(OR)_3 \xrightarrow{k^2_{epr}} \text{nonradical products}$$

The data can be represented by the Arrhenius equations (see Figure 1)

$$(k^2_{epr})_{R=Me} = 10^{9.3} \exp(-1750/RT) \quad M^{-1}\ sec^{-1} \qquad (I)$$

$$(k^2_{epr})_{R=Et} = 10^{8.8} \exp(-1700/RT) \quad M^{-1}\ sec^{-1} \qquad (II)$$

with the activation energies in cal/mol.

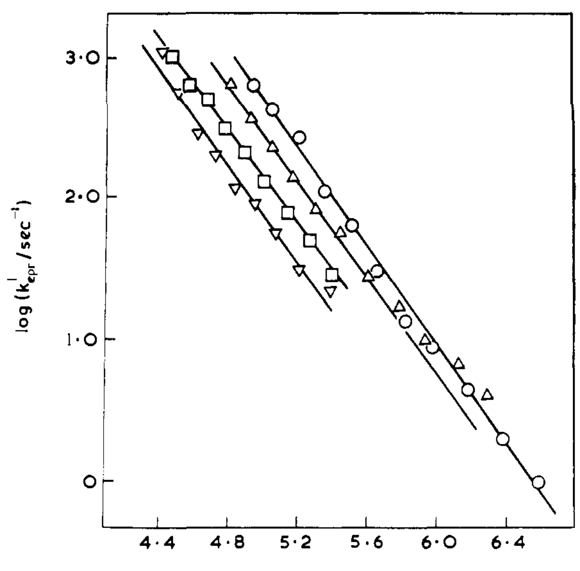


Figure 2. Log (k^1_{epr}/sec^{-1}) as a function of temperature for t-BuO$\dot{P}$(OMe)$_3$ (▽); t-BuO$\dot{P}$(OEt)$_3$ (□); t-BuO$\dot{P}$(OPr-i)$_3$ (△); and (t-BuO)$_4\dot{P}$ (○).

Unimolecular rate constants, k^1_{epr}, for the first-order decay of trialkoxy(*tert*-butoxy)phosphoranyl radicals have been plotted against the reciprocal of absolute temperature in Figure 2.

$$t\text{-BuO}\dot{P}(OR)_3 \xrightarrow{k^1_{epr}} \text{nonradical products}$$

The Arrhenius parameters are listed in Table III. The

Table III. First-Order Decay of Trialkoxy(*tert*-butoxy)phosphoranyl Radicals in Propane. Activation Parameters and Rate Constants at −60° by Direct Decay Rate Measurements

Phosphoranyl	Log (A^1_{epr}/sec^{-1})	E^1_{epr}, kcal/mol	k^1_{epr} × 10^{-2} at −60°, sec^{-1}
t-BuO$\dot{P}$(OMe)$_3$	10.5	7.9	2.4
t-BuO$\dot{P}$(OEt)$_3$	10.3	7.5	4.2
t-BuO$\dot{P}$(OPr-i)$_3$	10.8	7.7	8.5[a]
(t-BuO)$_4\dot{P}$	11.3	7.9	16[a]

[a] Extrapolated value. Error limits on log (A^1_{epr}/sec^{-1}) are ±0.5 and on E^1_{epr}, kcal/mol, ±0.5.

data for triethoxy(*tert*-butoxy)phosphoranyl are in rather poor agreement with the expression

$$(k_\beta)_{R=Et} = 10^{13.75} \exp(-10340/RT) \quad sec^{-1}$$

derived for the β scission of this radical by Davies, Griller, and Roberts[12] from steady-state measurements of phosphoranyl and *tert*-butyl radical concentrations in cyclopentane.

$$t\text{-BuO}\dot{P}(OEt)_3 \xrightarrow{k\beta} t\text{-Bu}\cdot + OP(OEt)_3$$

Since there is a possibility that k^1_{epr} and k_β represent different processes, the steady-state method was used to measure k_β for the four phosphoranyl radicals in propane and in a few other hydrocarbon solvents.

Steady-State Measurements. Under continuous irradiation the following reaction scheme is expected to apply.

Table IV. Rate Constant Ratios and Rate Constants at −60° Derived from Steady-State Measurements on t-BuO$\dot{P}$(OR)$_3$ Radicals[a]

R	Solvent[b]	Viscosity, cP[c]	$2k_t/k_\beta \times 10^{-6}\ M^{-1}$	$2k_t/k_x$	$k_\beta \times 10^{-2}$ sec^{-1} [d]	$k_x \times 10^{-8}$, M^{-1} sec^{-1} [d]
Me	Cyclopropane	0.18	13	2.3	1.2	7.0
Me	Propane	0.26	20	4.6	0.8	3.5
Me	Isooctane	1.2	15	*e*	1.1	
Me	Isooctane[f]	1.2	14	*e*	1.1	
Me	None[g]		4.0	3.6	4.0	4.4
Et	Cyclopropane	0.18	5.2	5.7	3.1	2.8
Et	Propane	0.26	6.3	*e*	2.5	
Et	Cyclopentane	1.2	8.9[h]	*e*	1.8	
Et	Isooctane	1.2	1.7	*e*	9.4	
Et	Toluene	1.7	1.1	8.0	14.5	2.0
i-Pr	Cyclopropane	0.18	1.0	2.8	16	5.7
i-Pr	Propane	0.26	1.8	6.8	8.9	2.4
i-Pr	Isooctane	1.2	0.3	2.5	53	6.4
t-Bu	Cyclopropane	0.18	5.3	*e*	3.0	
t-Bu	Propane	0.26	7.1	*e*	2.3	
t-Bu	Isooctane	1.2	1.4	*e*	1.1	

[a] The rate constant ratios are taken at −60° from the best line through experimental points measured over a temperature range of about 50–60°. The temperature of −60° was chosen because measurements were made at this temperature with all four phosphoranyl radicals. [b] Phosphite:peroxide:solvent, 1:1:3 by volume unless otherwise noted. [c] Viscosity of the neat solvent at −60°. Estimated value for cyclopropane R. W. Gallant, *Hydrocarbon Process.*, **49**, 137 (1970), and for isooctane H. Tschamler, F. Wettig, and E. Richter, *Monatsh. Chem.*, **80**, 572 (1949); J. M. Geist and M. R. Cannon, *Ind. Eng. Chem., Anal. Ed.*, **18**, 611 (1946). Data for cyclopentane, isobutane, propane, and toluene: "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," American Petroleum Research Project 44, Carnegie Press, Pittsburgh, Pa., 1963. [d] Taking $2k_t = 1.6 \times 10^9\ M^{-1}$ sec^{-1} at −60° (see text). [e] Intercept too small to calculate $2k_t/k_x$. [f] Phosphite:peroxide:isooctane, 1:1:18. [g] Phosphite:peroxide, 1:1. [h] From ref 12.

$$t\text{-BuOOBu-}t \xrightarrow{h\nu} 2t\text{-BuO}\cdot \qquad (1)$$

$$t\text{-BuO}\cdot + \mathrm{P(OR)_3} \longrightarrow t\text{-BuO}\dot{\mathrm{P}}\mathrm{(OR)_3} \qquad (2)$$

$$t\text{-BuO}\dot{\mathrm{P}}\mathrm{(OR)_3} \xrightarrow{k_\beta} t\text{-Bu}\cdot + \mathrm{OP(OR)_3} \qquad (3)$$

$$\left.\begin{array}{r} t\text{-Bu}\cdot + t\text{-Bu}\cdot \xrightarrow{2k_t} \quad (4) \\ t\text{-Bu}\cdot + t\text{-BuO}\dot{\mathrm{P}}\mathrm{(OR)_3} \xrightarrow{k_x} \quad (5) \\ 2t\text{-BuO}\dot{\mathrm{P}}\mathrm{(OR)_3} \xrightarrow{k^2_{\mathrm{epr}}} \quad (6) \end{array}\right\} \text{nonradical products}$$

Radical–radical reactions involving *tert*-butoxy radicals should be quite unimportant because their high rate of reaction with phosphite[12] (reaction 2, which is essentially irreversible[18]) keeps their steady-state concentration low. This reaction scheme yields

$$d[\mathrm{B}\cdot]/dt = 0 = k_\beta[\mathrm{P}\cdot] - 2k_t[\mathrm{B}\cdot]^2 - k_x[\mathrm{B}\cdot][\mathrm{P}\cdot]$$

where B· represents t-Bu· and P· represents t-BuO$\dot{P}$(OR)$_3$. This equation can be written as

$$\frac{1}{[\mathrm{B}\cdot]} = \frac{2k_t[\mathrm{B}\cdot]}{k_\beta[\mathrm{P}\cdot]} + \frac{k_x}{k_\beta}$$

At any particular temperature a plot of 1/[B·] against [B·]/[P·] should yield a straight line of slope $2k_t/k_\beta$ and intercept k_x/k_β. The relative magnitudes of [B·] and [P·] can be altered by changes in the incident light intensity. Experimentally it is found that under most conditions [B·] is approximately proportional to $(h\nu)^{0.5}$ and [P·] approximately proportional to $(h\nu)^{1.0}$. In general plots of this type yielded good straight lines.

For the t-BuO$\dot{P}$(OEt)$_3$ radical in cyclopentane the intercepts on the 1/[B·] axis (*i.e.*, k_x/k_β) were zero at most temperatures within the limits of experimental error.[12,23] By contrast, in the present work quite definite intercepts were obtained with this phosphoranyl and with t-BuO$\dot{P}$(OMe)$_3$ and with t-BuO$\dot{P}$(OPr-i)$_3$ in most solvents at the lower temperatures at which each was examined. The magnitude of the intercept increased as the temperature decreased. This implies that the cross reaction 5 becomes more important as the temperature is lowered. This is to be expected because the phosphoranyl radical concentration increases relative to the *tert*-butyl concentration as the temperature is lowered, and so the *tert*-butyl radicals are more likely to be trapped in reaction 5 than in their bimolecular self-reaction 4. That is, the activation energy for reaction 5 must be less than for reaction 3.

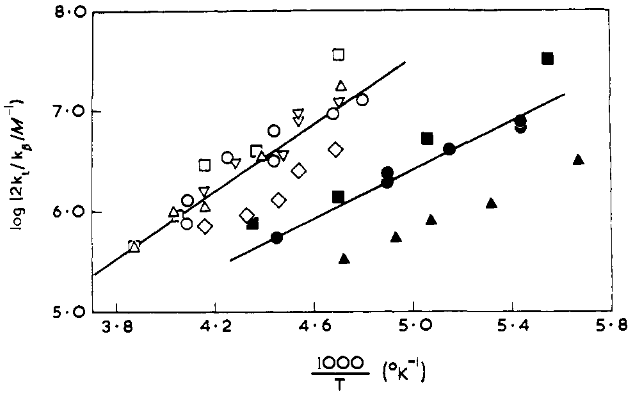


Figure 3. Log $(2k_t/k\beta/M^{-1})$ as a function of temperature. Open points refer to t-BuOP(OMe)$_3$ and filled points to t-BuO$\dot{P}$(OPr-i)$_3$. Phosphite–di-*tert*-butyl peroxide–solvent, 1:1:3 by volume; solvents–propane (□), cyclopropane (○), isooctane (△). Phosphite–peroxide–isooctane, 1:1:18 (▽). No solvent (◇).

Arrhenius plots of $2k_t/k_\beta$ derived from the slopes of the 1/[B·] *vs.* [B·]/[P·] lines are shown for two phosphoranyl radicals in various solvents in Figure 3, and values of $2k_t/k_\beta$ at −60° are listed in Table IV. For t-BuO$\dot{P}$(OMe)$_3$ there is little solvent effect except for the experiments done without a hydrocarbon diluent. For t-BuO$\dot{P}$(OPr-i)$_3$, $2k_t/k_\beta$ is noticeably smaller in isooctane than in propane or cyclopropane. Similar solvent effects were observed with t-BuO$\dot{P}$(OEt)$_3$ and

---

(23) Implying that $k_x < 10^8\ M^{-1}$ sec^{-1}.

with $(t\text{-BuO})_4\dot{\text{P}}$. The results suggest that $2k_t/k_\beta$ decreases with increasing solvent viscosity and that this effect is more pronounced as the mass of the phosphoranyl radical increases (see Table IV). The solvent viscosity effect cannot therefore result from changes in the value of $2k_t$. It seems unlikely that k_β could decrease with increasing solvent viscosity since there is no evidence that reaction 3 is reversible,[12,18] and therefore cage return should not occur even in very viscous media. As the phosphoranyl radicals become more massive there is broadening in the line shape of their epr spectra at a particular temperature. That is, $(t\text{-BuO})_4\dot{\text{P}}$ has a much higher proportion of the signal intensity in the wings of its epr lines than does $t\text{-BuO}\dot{\text{P}}(\text{OMe})_3$ for which most of the intensity is near the center of the lines. For the more massive radicals this broadening of the spectral lines becomes more pronounced with increasing solvent viscosity, presumably because the rate of rotation of the radicals decreases and this leads to anisotropic broadening of the spectra. It is possible that the phosphoranyl radical concentrations calculated by double integration of the epr derivative spectra underestimate the true radical concentrations when the lines become broad, because absorption in the wings increases relative to absorption at or near the center. While we are reluctant to attribute the entire solvent effect to line broadening and consequent error in the measurement of phosphoranyl concentrations it does seem likely that this is the main cause of the effect.

Arrhenius parameters derived from $2k_t/k_\beta$ values obtained in cyclopropane and propane are listed in Table V. They are, as is unfortunately always the case, much less reliable than the actual values of $2k_t/k_\beta$ determined near the center of the temperature range used in each study. The parameters for the other solvents have not been listed because the higher viscosity of these solvents has probably further diminished the accuracy of the measurements.

Table V. Arrhenius Parameters[a] for $2k_t/k_\beta$ in Cyclopropane and Propane

	Cyclopropane		Propane	
Phosphite	Log $(2A_t/A_\beta)$	$E_t - E_\beta$	Log $(2A_t/A_\beta)$	$E_t - E_\beta$
$(\text{MeO})_3\text{P}$	0.3	−6.5	−4.0	−11.5
$(\text{EtO})_3\text{P}$	0.7	−5.9	−1.1	−7.7
$(i\text{-PrO})_3\text{P}$	0.7	−5.2	−0.6	−6.7
$(t\text{-BuO})_3\text{P}$	1.0	−5.5	0.4	−6.5

[a] Units of A_t are M^{-1} sec^{-1}, of A_β sec^{-1}, and of E_t and E_β kcal/mol. Error limits on log $(2A_t/A_\beta)$ are ±1.0 and on $(E_t - E_\beta)$, ±1.0.

The results listed in Tables III and V can be combined on the reasonable assumption that $A^1{}_{\text{epr}} = A_\beta$ and $E^1{}_{\text{epr}} = E_\beta$. For statistical reasons the preexponential factor for the formation of *tert*-butyl is expected to be larger by a factor of four (0.6 log unit) for $(t\text{-BuO})_4\dot{\text{P}}$ than for the other three phosphoranyl radicals. After correcting for this statistical factor the mean value of log $(A^1{}_{\text{epr}}/\text{sec}^{-1})$ is 10.6. Combining this with the data in Table V, exclusive of that for $t\text{-BuO}\dot{\text{P}}(\text{OMe})_3$ in propane which is clearly anomalous (see also Figure 3), yields a mean value for log $(2A_t/M^{-1}\ \text{sec}^{-1}) = 11.0$ in reasonable agreement with the value of 10.7 used in previous work[12] and with the value of 10.2 ± 0.4 measured directly by kinetic epr spectroscopy.[24] A similar combination of the individual values of $E^1{}_{\text{epr}}$ with the values of $E_t - E_\beta$ yields an average value for E_t of 1.5 kcal/mol which is also in good agreement with the 2.0 kcal/mol used previously[12] and with the value of 1.0 ± 0.4 kcal/mol measured directly.[24] There would seem to be little doubt that $k^1{}_{\text{epr}}$ and k_β correspond to virtually identical processes. The only likely source of difference between these two rate constants is that $k^1{}_{\text{epr}}$ can contain a contribution from reaction 5, the cross $\text{B}\cdot + \text{P}\cdot$ reaction. The importance of reaction 5 increases with decreasing temperature.

Plots of log (k_x/k_β) against $1/T$ (°K) yield straight lines which, within the rather large experimental error, are parallel with those for the log $(2k_t/k_\beta)$ against $1/T$ (°K) graphs. This indicates that $E_x \simeq E_t \simeq 1.0$ kcal/mol. Values of $2k_t/k_x$ (from the ratio of slope to intercept in the $1/[\text{B}\cdot]$ against $[\text{B}\cdot]/[\text{P}\cdot]$ plots) at −60° are listed in Table IV, when the intercepts were sufficiently large to be determined. The k_x values at −60° listed in this table have been calculated on the basis[24] of $2k_t = 1.6 \times 10^9\ M^{-1}\ \text{sec}^{-1}$ at this temperature.

The phosphoranyl radical derived from the reaction of *tert*-butoxy with 2-methoxy-1,3,2-dioxaphosphorinan undergoes two different β-scissions,[15] a *tert*-butyl elimination, and a scission of the dioxaphosphorinan ring to yield a substituted *n*-alkyl radical. For this reason the value of k_β for *tert*-butyl formation could not be obtained by the steady-state method. However the temperature range in which both *tert*-butyl and the phosphoranyl radical could be observed was similar to the ranges used in studying the trialkoxy(*tert*-butoxy)phosphoranyl radicals. The rate constant for *tert*-butyl elimination from the $t\text{-BuO(MeO)}\overline{\dot{\text{P}}\text{O(CH}_2)_3\text{O}}$ radical must therefore be of similar magnitude to that found for the $t\text{-BuO}\dot{\text{P}}(\text{OR})_3$ radicals.

Discussion

The most interesting feature of the present results is the similarity of the rate constants for β-scission of the four trialkoxy(*tert*-butoxy)phosphoranyl radicals studied. Steric effects cannot therefore be of major importance in this series of radicals, though they are known to play some role in the β scission of certain other tetraalkoxyphosphoranyl radicals.[15,26] Presumably the alkyl groups are sufficiently well separated that interaction between them is not large. The small increase in $a(^{31}\text{P})$ with increasing size of alkyl groups (see Table I) suggests however, that there may be sufficient interaction to cause some distortion in the geometry of the radicals.

The similarity in the rate constants for β-scission of tetraalkoxyphosphoranyls does not extend to radicals from which an alkyl radical other than *tert*-butyl is eliminated. Thus,[15] the $(\text{EtO})_4\dot{\text{P}}$ radical is much more

---

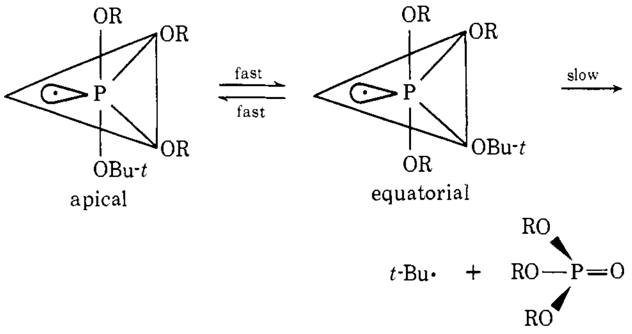
[24] Measured over a temperature range from −11 to −85° in isobutane-di-*tert*-butyl peroxide, 10:1 and 5:1 by volume, systems which should be of comparable viscosity to the propane and cyclopropane reaction mixtures. (The viscosity of isobutane at −60° is 0.44 cP). These new measurements indicate that a previously reported value for $2k_t$ at room temperature[25] is too large by a factor of about 3, probably because the epr signal of the *tert*-butyl radical was partially saturated under the conditions of the earlier experiments.

[25] G. B. Watts and K. U. Ingold, *J. Amer. Chem. Soc.*, **94**, 491 (1972).

[26] D. H. R. Barton, T. J. Bentley, R. H. Hesse, F. Mutterer, and M. M. Pechet, *Chem. Commun.*, 912 (1971).

stable than the $t\text{-BuO}\dot{\text{P}}\text{(OEt)}_3$ since it has to eliminate an ethyl, which is much less stable than a *tert*-butyl radical. In contrast the reaction of benzyloxy radicals (from the photolysis of benzyl hyponitrite) with $\text{(EtO)}_3\text{P}$ yielded only benzyl radicals (see introductory section and ref 19). No phosphoranyl could be detected in cyclopropane at the lowest temperatures at which some hyponitrite remained in solution (*ca.* −60°). Similarly, the reaction of *tert*-butoxy with triallyl phosphite yields only allyl radicals. No phosphoranyl could be detected in propane even at −140°. The rapidity of both these β-scissions is due to the considerable resonance stabilization of benzyl and allyl radicals.[27]

After correcting for statistical factors the mean value of A^1_{epr} $(=A_\beta)$ is $10^{10.6}$ sec^{-1} which is quite small for a unimolecular reaction[28] and implies that a fairly complex rearrangement is involved. Phosphoranyl radicals probably have a slightly distorted trigonal-bipyramidal structure, with the orbital containing the unpaired electron occupying a position in the equatorial plane.[12,13,16] It seems likely that β-scission occurs from the equatorial position since the stability of alkoxyalkylphosphoranyls, $\text{(R'O)}_n\dot{\text{P}}\text{R}_{4-n}$, is apparently maximized when $n = 2$.[13,29] The two alkoxy groups are expected to take up the apical positions and the two alkyl groups the equatorial positions since the more electronegative groups prefer the apical positions in analogous five-coordinate phosphoranes.[30] If β-scission occurred from the apical position the $\text{(R'O)}_2\dot{\text{P}}\text{R}_2$ radicals would be expected to be as unstable as $\text{(RO)}_4\dot{\text{P}}$ radicals, whereas they decay with lifetimes of minutes[13] rather than milliseconds. The overall process can be represented as



There is evidence in the "ponderal" effect[15,26] that steric factors can influence β-scission. That is, in an unsymmetrically substituted tetraalkoxyphosphoranyl the smaller alkyl radical is preferentially eliminated *provided* the stabilities of the various possible alkyl radicals are similar. Since $(t\text{-BuO})_4\dot{\text{P}}$ is not much more reactive than the other three phosphoranyls there cannot be much preference for the bulky *tert*-butoxy to lie in an apical position in the $t\text{-BuO}\dot{\text{P}}\text{(OR)}_3$ radicals. The absence of a large steric effect on k^1_{epr} $(=k_\beta)$ suggests that the expected steric influence on radical conformation may be counterbalanced by an opposing electronic factor. That is, inductive electron release by alkyl groups increases along the series Me < Et < *i*-Pr < *t*-Bu and hence *tert*-butoxy might on electronic grounds[30] be expected to prefer an equatorial position. The general similarity in k^1_{epr} values suggests either that the opposing steric and electronic effects are quite nicely balanced in these four phosphoranyls or that the influence of both is quite small.

The presence in $t\text{-BuO(MeO)}\overline{\dot{\text{P}}\text{O(CH}_2\text{)}_3\text{O}}$ of a ring system might be expected to reduce the rate of pseudorotation of this phosphoranyl. If this occurs it does not have much effect on the rate of loss of *tert*-butyl from this phosphoranyl since the rate of this mode of β-scission is similar to that for the trialkoxy(*tert*-butoxy)phosphoranyls.

The reaction of *tert*-butyl radicals with phosphoranyl radicals appears to be subject to steric effects, since the reaction was not observed with $(t\text{-BuO})_4\dot{\text{P}}$ (see k_x values in Table IV). As we might expect,[28] the rate constants for these cross reactions are not too far removed from the geometric mean of the rate constants for the bimolecular self-reactions of the individual radicals, *viz.* for $\text{B}\cdot + \text{B}\cdot$, $2k_t = 1.6 \times 10^9\ M^{-1}\ \text{sec}^{-1}$ at −60° and for $\text{P}\cdot + \text{P}\cdot$, $k^2_{\text{epr}} = 3 \times 10^7\ M^{-1}\ \text{sec}^{-1}$ for $t\text{-BuO}\dot{\text{P}}\text{(OMe)}_3$, and $1 \times 10^7\ M^{-1}\ \text{sec}^{-1}$ for $t\text{-BuO}\dot{\text{P}}\text{(OEt)}_3$ in propane at −60° (calculated from Arrhenius equations I and II). The reaction may be a combination since some alkoxyalkylphosphoranes are known,[31] *i.e.*

$$t\text{-Bu}\cdot + t\text{-BuO}\dot{\text{P}}\text{(OR)}_3 \longrightarrow t\text{-Bu}(t\text{-BuO})\text{P(OR)}_3$$

or perhaps a disproportionation,[32] *i.e.*

$$t\text{-Bu}\cdot + t\text{-BuO}\dot{\text{P}}\text{(OR)}_3 \longrightarrow t\text{-BuH} + \text{(CH}_3\text{)}_2\text{C=CH}_2 + \text{OP(OR)}_3$$

There is a noticable steric hindrance to the bimolecular self-reaction of phosphoranyl radicals (*cf.* Table II), a process which presumably yields P–P coupled dimers stable at the low temperatures where this reaction is observed.

$$2t\text{-BuO}\dot{\text{P}}\text{(OR)}_3 \longrightarrow t\text{-BuO(RO)}_3\text{P—P(OR)}_3\text{OBu-}t$$

Acknowledgment. The authors are pleased to acknowledge many helpful discussions with Dr. B. P. Roberts and Professor A. G. Davies during the course of this work. One of us (D. G.) thanks the S.R.C. for a studentship during which this work was carried out.

---

(27) An exceptionally short phosphoranyl radical lifetime may explain the stereoselectivity observed by Bentrude and Min.[19]

(28) S. W. Benson, "Thermochemical Kinetics," Wiley, New York, N. Y., 1968.

(29) R. W. Dennis, unpublished results. α scission does however occur from the apical position.

(30) E. L. Muetterties, W. Mahler, and R. Schmutzler, *Inorg. Chem.*, 2, 613 (1963); E. L. Muetterties, W. Mahler, J. K. Packer, and R. Schmutzler, *ibid.*, 3, 1298 (1964); P. Gillespie, P. Hoffman, H. Khusacek, D. Marquarding, S. Pfohl, F. Ramirez, E A. Tsolis, and I. Ugi, *Angew. Chem., Int. Ed. Engl.*, 10, 687 (1971).

(31) D. B. Denney, D. Z. Denney, B. C. Chang, and K. L. Marsi, *J. Amer. Chem. Soc.*, 91, 5243 (1969).

(32) *Cf.* R. S. Davidson, *Tetrahedron*, 25, 3383 (1969).