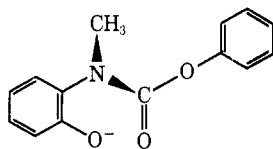ion lies immediately adjacent to the carbonyl so that perpendicular attack can readily occur.[22] Thus, the stereochemistry imposed on the molecule is such as to facilitate greatly the intramolecular nucleophilic reaction.

While other factors can also influence intramolecular catalysis, it appears reasonable that proper orientation is at least partly responsible for the efficient reaction in the present case.

Extremely large effective molarities in reactions of neighboring groups with ester functions have only been previously reported for carboxylate ions[5] (10^8 M), and so far, no comparable values have been found for neighboring nitrogen bases.[2-4] With neighboring pyridine in (para-substituted phenyl)ethylpyridine carbonate the effective molarity varies from 30 to 50 M, depending upon the substituent.[23] The largest effective molarity found to date for a nitrogen base is 5 × 10^3 M in the case of the dimethylamino group of p-nitrophenyl γ-dimethylaminobutyrate.[4] Therefore, it is possible that effective molarities of 10^8 M are characteristic of anionic nucleophiles. A possibility is that desolvation of highly solvated anionic nucleophiles is a

requirement in intermolecular reactions, but not in intramolecular reactions where water molecules cannot fit between the nucleophilic group and the reaction center. The energy requirement for desolvation of an anion should be considerable.[24] Bruice and Turner[7] found that effective molarities of neighboring carboxyl did not vary greatly on changing the solvent from H_2O to 1 M H_2O–DMSO. However, it is not certain that a carboxyl group would be completely desolvated in 1 M H_2O–DMSO. Hydroxide ion is still highly solvated in that solvent.[25]

The fact that an oxide ion is an excellent intramolecular nucleophile when held adjacent to the carbonyl group is of interest in regard to the mechanism of action of esteratic enzymes having serine at the active site. The generally accepted mechanism for acylation of α-chymotrypsin involves histidine-57 general-base assisted acylation of serine-195.[2] In this mechanism a proton is partially removed from the serine hydroxyl group as it attacks the carbonyl group of the substrate. It is clear that a serine oxygen should be a powerful nucleophile in an intracomplex reaction towards an ester substrate where the carbonyl is bound in close proximity to the serine hydroxyl.

(22) M. L. Bender, *Chem. Rev.*, 60, 63 (1960).
(23) J. E. C. Hutchins and T. H. Fife, unpublished data.
(24) K. D. Gibson and H. Scheraga, *Proc. Nat. Acad. Sci. U. S.*, 58, 420 (1967).
(25) R. Goitein and T. C. Bruice, *J. Phys. Chem.*, 76, 432 (1972).

Free-Radical Chemistry of Organophosphorus Compounds. III. α vs. β Scission in Reactions of Alkoxy and Thiyl Radicals with Trivalent Organophosphorus Derivatives

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Abstract: Reactions of a series of X–P(OEt)$_2$ (where X = Cl, alkyl, Ph, PhO, AcO, and n-Bu$_2$N) with alkoxy and thiyl radicals (RA·, A = O or S) have been studied to attempt to understand more fully the factors which determine the relative amounts of oxidation [APX(OEt)$_2$] and displacement [RAP(OEt)$_2$] products which result in such systems. With A = O, both oxidation and displacement take place depending on the natures of R and X. Displacement as well as oxidation also is noted in a few instances with A = S when the P–X bond is relatively weak. Analysis of our findings along with those of other workers leads to the conclusion that to a first approximation the relative strengths of the R–A and P–X bonds in the probable phosphoranyl radical intermediates, RAPX-(OEt)$_2$, determine the proportions of α-scission (displacement) and β-scission (oxidation) processes which occur. Inclusion of substituents in a five-membered ring [MeOP(OCH$_2$)$_2$] does not result in ring opening. Possible more subtle refinements of these ideas, which await experimental testing, are also presented.

Reactions of alkoxy or thiyl radicals with trivalent phosphorus compounds potentially may be divided into two distinct types, displacements (eq 1a) and oxidations (eq 1b). In terms of the phosphoranyl radical 1 which may be an intermediate in both pathways, the processes which lead to displacement or oxidation products may be classified respectively as α scission (eq

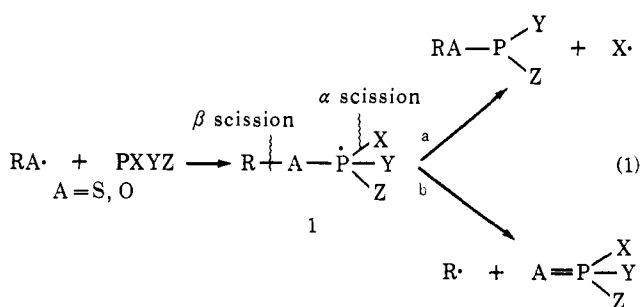1a) and β scission (eq 1b). That both oxidations and displacements do in fact occur experimentally with A = O was noted in early studies of such systems; e.g., reaction of n-Bu$_3$P with *tert*-butoxy radicals from di-*tert*-butyl peroxide decomposition at 130° gave[1] displace-
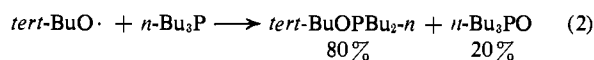
(1) S. A. Buckler, *J. Amer. Chem. Soc.*, 84, 3093 (1962).

Table I. α vs. β Scission in Reactions of RO· with PXYZ

Case	RO·, [M]	X	Y	Z	Temp, °C	Solvent[a]	—Yield products, %— ROPYZ[b]	O=PXYZ	Oxidation/ Displacement	$\bar{D}_{PX_3}$,' kcal/mol
1	tert-BuO, [0.220, 0.222][c]	Et	OEt [0.552, 0.551][c]	OEt	65	C₆H₆	86, 86	0, 0	0	62
2	tert-BuO, [0.482, 0.490][c]	tert-Bu	OEt [0.258, 0.254][c]	OEt	65	C₆H₆	82, 79	0, 0	0	d
3	tert-BuO, [0.713, 0.690][c]	PhCH₂	OEt [0.222, 0.216][c]	OEt	65	C₆H₆	81, 82[j]	0, 0	0	48[e]
4	tert-BuO, [0.58]	n-Bu₂N	OEt [0.497]	OEt	65	C₆H₆	84[k]	3.9	0.046	59–69
5	tert-BuO, [0.45]	PhO	OEt [0.523]	OEt	65	C₆H₆	95[l]	2.7	0.028	69–74[f]
6	tert-BuO, [0.498]	Cl	OEt [0.562]	OEt	65	C₆H₆	36	41	1.1	77
7	tert-BuO, [0.66]	AcO	OEt [0.500]	OEt	65	C₆H₆	0	84	∞	<84[g]
8	tert-BuO, [0.38]	MeO	OCH₂ [0.39]	CH₂O	65	C₆H₆	0	93	∞	~84[h]
9	tert-BuO, [0.200]	Ph	OMe [0.218]	OMe	65	C₆H₆	0	99	∞	77
10	PhCH₂O, [0.158, 0.170][c]	Me	OEt [0.0897, 0.0904][c]	OEt	60	C₆H₆	20, 18	57, 54	2.9, 2.9	67
11	PhCH₂O, [0.160, 0.163][c]	Et	OEt [0.0813, 0.0850][c]	OEt	60	C₆H₆	56, 55	11, 11	0.19, 0.19	62
12	PhCH₂O, [0.170, 0.165][c]	tert-Bu	OEt [0.0786, 0.0760][c]	OEt	60	C₆H₆	58, 52	3.2, 3.7	0.055, 0.071	d
13	PhCH₂O, [0.160, 0.165][c]	PhCH₂	OEt [0.0792, 0.0820][c]	OEt	60	C₆H₆	67, 66	3.2, 3.2	0.048, 0.048	48[e]
14	PhCH₂O, [0.166, 0.16][c]	n-Bu₂N	OEt [0.0479, 0.049][c]	OEt	60	C₆H₆	36, 34[m]	61, 58	1.7, 1.7	59–69
15	PhCH₂O, [0.183, 0.166][c]	PhO	OEt [0.092, 0.083][c]	OEt	60	C₆H₆	13, 14[n]	84, 87	6.5, 6.2	69–74

[a] Degassed solutions. [b] Total yield ROPYZ plus ROP(O)YZ from subsequent tert-BuO· oxidation of ROPYZ. [c] Molar concentrations for two different runs. [d] Unknown. [e] Estimated from $\bar{D}_{PMe_3}$ and assumption of 19 kcal/mol resonance energy for PhCH₂· on the basis of the difference in bond dissociation energies for Me–H and PhCH₂–H (104 and 85 kcal/mol, respectively: J. A. Kerr, *Chem. Rev.*, **66**, 465 (1966)). Therefore, the $\bar{D}_{P(CH_2Ph)_3}$ is estimated to be 19 kcal/mol less than $\bar{D}_{PMe_3}$ (67 kcal/mol: J. D. Cox and G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds," Academic Press, New York, N. Y., 1970). [f] Assuming resonance energy of PhO· is 10–15 kcal/mol. [g] Will depend on resonance energy of AcO·. [h] Effect of ring of $\bar{D}_{P-O}$ not known. [i] From Table IV except as noted. [j] Yield of PhCH₂CH₂Ph: 105%, based on ROPYZ. [k] Yield of n-Bu₂NH: 82, 86% based on ROPYZ. [l] Yield of PhOH: 22, 24% based on ROPYZ. [m] n-Bu₂NH present but not assayed quantitatively. [n] Yield of PhOH: 73, 83% based on ROPYZ (all of yields in i-n by glc analysis).

$$RA· + PXYZ \longrightarrow R + A—P\underset{Z}{\overset{X}{\diagdown Y}} \quad (1)$$

A = S, O

ment/oxidation in a 4/1 ratio as shown by eq 2. By con-

$$tert\text{-BuO·} + n\text{-Bu}_3P \longrightarrow tert\text{-BuOPBu}_2\text{-}n + n\text{-Bu}_3PO \quad (2)$$
$$80\% \qquad 20\%$$

trast, reaction of tert-butoxy radicals with triphenylphosphine was found to give triphenylphosphine oxide exclusively.[2] The same was noted with triethyl phosphite.[3] Thiyl radicals (A = S) were found to give oxidation exclusively with all of the above.[2–4] It is significant that in this, as in other such competitions, the displacement process is *thermodynamically much less favored than oxygen or sulfur transfer.*

(2) C. Walling, O. H. Basedow, and E. S. Savas, *J. Amer. Chem. Soc.*, **82**, 2181 (1960).
(3) C. Walling and R. Rabinowitz, *ibid.*, **81**, 1243 (1959).
(4) C. Walling and M. Pearson, *ibid.*, **86**, 2262 (1964).

This paper reports results[5] of our efforts to understand what the important factors are which determine for a given set of reactants [reaction scheme 1] whether oxidation or displacement will predominate. Our results along with those of other workers are interpreted in terms of the intermediate **1** with the conclusion that the competition between α and β scission is determined *primarily* by the relative strengths of the R–A and P–X bonds. Other factors which could be important are also discussed.

Results

Reactions between a variety of X–P(OEt)₂ and certain alkoxy and thiyl radicals were carried out in the temperature range 60–80°. Dibenzyl[6] and tert-butyl hyponitrites[7] were decomposed thermally as a source of PhCH₂O· and tert-BuO·, respectively. Thiyl radicals were generated from the corresponding thiols using azobisisobutyronitrile as initiator. The reaction sequence generally proposed for such oxidations using RSH is[3,8]

(5) Part of this work appeared in preliminary form: W. G. Bentrude, E. R. Hansen, W. A. Khan, and P. E. Rogers, *ibid.*, **94**, 2867 (1972).
(6) J. R. Partington and C. C. Shah, *J. Chem. Soc.*, 2595 (1932); S. K. Ho and J. B. de Sousa, *ibid.*, 1788 (1961).
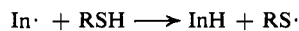(7) H. Kiefer and T. G. Traylor, *J. Amer. Chem. Soc.*, **89**, 6667 (1967); H. Kiefer and T. G. Traylor, *Tetrahedron Lett.*, 6163 (1966).
(8) R. D. Burkhart, *J. Phys. Chem.*, **70**, 605 (1966); C. Walling and R. Rabinowitz, *J. Amer. Chem. Soc.*, **79**, 5326 (1957).

Table II. α vs. β Scission in Reactions of RS· with PXYZ

Case	RS·, [M]	X	Y	Z	Temp, °C	Solvent[b]	Yield products, % RSPYZ	S=PXYZ	Displacement/Oxidation	$\bar{D}_{PX_3}$[h]
1	tert-BuS, [0.264, 0.260][a]	Et	OEt [0.601, 0.602][a]	OEt	65	C6H6	0	87, 86	0	62
2	tert-BuS, [0.259, 0.259][a]	tert-Bu	OEt [0.468, 0.492][a]	OEt	65	C6H6	0	94, 92	0	j
3	i-PrS, [1.9]	tert-Bu	OEt [0.35]	OEt	60	o-Cl2C6H4	4.0[c]	86	0.046	j
4	i-PrS, [1.9]	PhCH2	OEt [0.35]	OEt	60	o-Cl2C6H4	31[c]	63	0.48	48[d]
5	tert-BuS, [1.8]	PhCH2	OEt [0.35]	OEt	60	o-Cl2C6H4	16[i]	76	0.21	48[d]
6	p-MeC6H4CH2S, [1.3]	PhCH2	OEt [0.35]	OEt	60	o-Cl2C6H4	6.5[i]	86	0.076	48[d]
7	tert-BuS, [0.575]	n-Bu2N	OEt [0.53]	OEt	65	C6H6	0.0	98	0	59–69
8	tert-BuS, [0.49]	PhO	OEt [0.484]	OEt	65	C6H6	0.0	97	0	69–74[e]
9	tert-BuS, [1.00]	Cl	OEt [0.510]	·OEt	65	C6H6	0.0	95	0	77
10	tert-BuS, [1.02]	AcO	OEt [0.522]	OEt	65	C6H6	0.0	93	0	f
11	tert-BuS, [0.56]	MeO	OCH2 [0.400]	CH2O	65	C6H6	0.0	96	0	~84[g]
12	tert-BuS, [0.63]	Me2N	Me2N [0.543]	Me2N	65	C6H6	0.0	95	0	59–69

[a] Molar concentrations of reactants, duplicate runs. [b] Degassed solutions. [c] Analyzed by vpc as RSP(S)YZ. [d] Estimated from $\bar{D}_{P-C}$ for PMe₃ and assumed 19 kcal/mol stabilization energy for PhCH₂· : J. A. Kerr, *Chem. Rev.*, **66**, 465 (1966). [e] Assumed 10–15 kcal/mol resonance energy for PhO·. [f] Unknown, depends on resonance energy of AcO·. [g] Effect of ring on $\bar{D}_{P-O}$ not known. [h] From Table IV except as noted. [i] Measured as toluene, near-quantitative amounts of RSP(S)(OEt)₂ also present (glc). [j] Not known.

$$In· + RSH \longrightarrow InH + RS·$$

$$RS· + PXYZ \longrightarrow RSPXYZ \longrightarrow R· + S=PXYZ$$

$$R· + RSH \longrightarrow RH + RS·$$

The rates of thiyl radical reactions were very slow in control reactions in which initiator was not present. Oxygen was excluded from all reactions either by freeze–thaw degassing methods or by purging with pure nitrogen. Control reactions with the alkoxy radical source excluded showed less than 2% of oxide to be formed. Reactant concentrations, solvent, reaction temperatures, and absolute yields of products from the alkoxy radical reactions are found in Table I. Reactions with PhCH₂O· were carried out with excess alkoxy radical so that a major part if not all of the product ROPYZ was analyzed as ROP(O)YZ. Evidence for the free-radical nature of the PhCH₂O· oxidations stems from the formation of bibenzyl in yields 50–60% based on moles of oxides formed. Products of reaction of the radical X· from displacement were also found in some instances as noted in the footnotes of Table I. Table II records the results for the thiyl radical systems using *excess* RSH in most cases. Displacement products, RSPYZ, were analyzed, therefore, as the corresponding sulfides, RSP(S)YZ. Alternately, product hydrocarbon, XH, from hydrogen abstraction by displaced X· was used to assess the yield of displacement product. Yields in Tables I and II were determined by vpc using the internal standard method with sensitivity corrections and are based on PXYZ consumed.

In Table III are compiled results of studies by other workers in systems where either displacement or oxidation could occur. Cases in which oxidation or displacement accounted for greater than 10% of the total products formed are indicated with a plus (+).

Discussion

Phosphoranyl radicals, ·PZ₄, were first observed by esr as the perhalo compounds F₄P·[9] and Cl₄P·[10] and generally appear to have a trigonal-bipyramidal structure[11] with the odd electron equatorial. Over the past few years a number of such species containing organic substituents on phosphorus also have been characterized by esr. In fact, the whole range (x = 0 to 3) of alkyl–alkoxy intermediates of type $R_x'P(OR)_{4-x}$ from reaction of radicals with trivalent phosphorus has been detected[12-14] on generation of alkoxy radicals in the presence of trivalent phosphorus compounds. Although it is not in this way *proved*, the esr results are consistent with the idea that phosphoranyl radicals are in fact intermediates in the oxidations and displacements which ensue. Therefore, we find it reasonable to discuss the competition between displacement and oxidation in terms of the competitive α- and β-scission processes available to the potential phosphoranyl radical intermediate. Figure 1 depicts for alkoxy radicals the formation of ROPXYZ and the competition between the

(9) (a) J. R. Morton, *Can. J. Phys.*, **41**, 706 (1963); (b) P. W. Atkins and M. C. R. Symons, *J. Chem. Soc.*, 4364 (1964); (c) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **45**, 1845 (1966); (d) W. Nelson, G. Jackel, and W. Gordy, *ibid.*, **52**, 4572 (1970).

(10) G. F. Kokoszka and F. E. Brinckman, *J. Amer. Chem. Soc.*, **92**, 1199 (1970); A. Begum and M. C. R. Symons, *J. Chem. Soc. A*, 2065 (1971); C. M. L. Kerr and F. Williams, *J. Phys. Chem.*, **75**, 3023 (1971).

(11) J. Higuchi, *J. Chem. Phys.*, **50**, 1001 (1969).

(12) (a) J. K. Kochi and P. J. Krusic, *J. Amer. Chem. Soc.*, **91**, 3944 (1969); (b) P. J. Krusic, W. Mahler, and J. K. Kochi, *ibid.*, **94**, 6033 (1972).

(13) A. G. Davies, R. W. Dennis, D. Griller, and B. P. Roberts, *J. Organometal. Chem.*, **40**, C33 (1972).
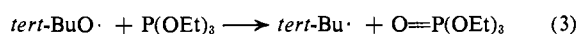
(14) (a) A. G. Davies, D. Griller, and B. P. Roberts, *Angew. Chem., Int. Ed. Engl.*, **10**, 738 (1971); (b) A. G. Davies, D. Griller, and B. P. Roberts, *J. Chem. Soc., Perkin Trans. 2*, 993 (1972); (c) G. B. Watts and K. U. Ingold, *J. Amer. Chem. Soc.*, **94**, 2528 (1972); (d) G. B. Watts, D. Griller, and K. U. Ingold, *ibid.*, **94**, 8784 (1972).

Table III. Literature Citations to α *vs.* β Scission in Reactions of RO· and RS· with PXYZ

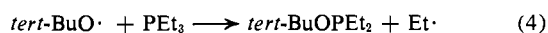| Case	RO· or RS·	X	Y	Z	Temp, °C	ROPYZ[a] or RSPYZ	O=PXYZ[a] or S=PXYZ	$\bar{D}_{PX_3}$[c]	Ref
1	*tert*-BuO	EtO	EtO	EtO	130	−	+	84	3
2	*tert*-BuO	Ph	Ph	Ph	130	−	+	77	2
3	*tert*-BuO	Me	Me	Me	< −80	+[b]	−	67	g
4	*tert*-BuO	Et	Et	Et	< −80	+[b]	−	62	g
5	*tert*-BuO	Et	Et	OEt	−96 to −128	+[b]	−	62	h
6	*tert*-BuO	*i*-Pr	*i*-Pr	*i*-Pr	< −80	+[b]	−	e	g
7	*tert*-BuO	*i*-Bu	*i*-Bu	*i*-Bu	< −80	+[b]	−	e	g
8	*tert*-BuO	c-C₆H₁₁	c-C₆H₁₁	c-C₆H₁₁	< −80	+[b]	−	e	g
9	*tert*-BuO	*n*-Bu	*n*-Bu	*n*-Bu	130	+[b]	+	62[d]	1
10	*tert*-BuO	CF₃	CF₃	CF₃	< −80	+[b]	−	e	g
11	*tert*-BuO	CH₃	*n*-Pr	Ph	65	−	+	62[d]	i
12	*tert*-BuO	(EtO)₂PO	EtO	EtO	−10 to −50	+	−	e	j
13	*tert*-BuO	PhO	Me	Me	< −70[b]	+	−	69–74[f]	g
14	*tert*-BuO	PhO	PhO	PhO	130	+	−	69–74[f]	k, 4
15	*tert*-BuO	Et₂P	Et	Et	−50[b]	+	−	50–70	g
16	(CF₃)₂NO·	Me₂N	Me₂N	Me₂N	−50	+	−	69	l
17	*i*-BuS	EtO	EtO	EtO	60–120	−	+	84	3, 8
18	*n*-BuS	*n*-Bu	*n*-Bu	*n*-Bu	60–70	−	+	62	2, 4
19	*n*-BuS	Ph	Ph	Ph	70	−	+	77	4
20	*n*-BuS	PhO	PhO	PhO	70	+	−	69–74[f]	4
21	MeS	Et₂P	Et	Et		+	−	50–70	m

[a] Comprised more (+) or less (−) than 10% of total product. Unless otherwise noted based on stable isolated or vpc analyzed products. [b] Based on detection by esr of displaced radical X· of radical from oxygen transfer, *tert*-Bu·. [c] Average bond energies from Table IV except as noted. [d] Value for Et₃P. [e] Unknown. [f] Assuming resonance energy of PhO· is 10–15 kcal/mol. [g] J. K. Kochi and P. J. Krusic, *J. Amer. Chem. Soc.*, **91**, 3944 (1969); P. J. Krusic, W. Mahler, and J. K. Kochi, *ibid.*, **94**, 6033 (1972). [h] A. G. Davies, R. W. Dennis, D. Griller, and B. P. Roberts, *J. Organometal. Chem.*, **40**, C33 (1972). [i] W. G. Bentrude, P. E. Rusek, Jr., and J. H. Hargis, *Chem. Commun.*, 5296 (1969). [j] A. G. Davies, D. Griller, and B. P. Roberts, *J. Amer. Chem. Soc.*, **94**, 1782 (1972). [k] W. G. Bentrude, *Tetrahedron Lett.*, 3543 (1965). [l] Y. O. E. Nigumi and H. J. Emeléus, *J. Inorg. Nucl. Chem.*, **32**, 3213 (1970). [m] Yu. N. Shlyk, G. M. Bogolybov, and A. A. Petrov, *J. Gen. Chem. USSR*, **38**, 194 (1968).

two scission steps for X = alkyl. The exothermicity of ·PZ₄ formation on reaction with an alkoxy radical is consistent with the known low overall E_a (1–3 kcal/mol) and irreversibility[15] of the reactions of *tert*-BuO· and PhCH₂O· with PXYZ (processes 3 and 4). (In another

$$\text{tert-BuO·} + \text{P(OEt)}_3 \longrightarrow \text{tert-Bu·} + \text{O=P(OEt)}_3 \quad (3)$$

[log k (M^{-1} sec^{-1}) = 9.83 − 2.24/2.303RT,[14a,b]

$$\Delta H \cong -57 \text{ kcal/mol}$$

$$\text{tert-BuO·} + \text{PEt}_3 \longrightarrow \text{tert-BuOPEt}_2 + \text{Et·} \quad (4)$$

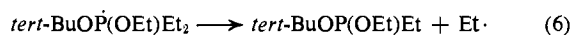[log k (M^{-1} sec^{-1}) = 9.34 − 1.34/2.303RT,[13]

$$\Delta H \cong -22 \text{ kcal/mol}$$

paper,[16] we have outlined our tentative interpretation of the reactivity trends in such systems in terms of the effects of the relative strength of the PZ bond formed and possible resonance interaction in ·PZ₄ on the thermodynamics of ·PZ₄ formation.) The heights of the α- and β-scission barriers are intended to correspond roughly to the rate expressions shown below which have been determined for processes 5 and 6.

$$\text{tert-BuOP(OEt)}_3 \longrightarrow \text{tert-Bu·} + \text{O=P(OEt)}_3 \quad (5)$$
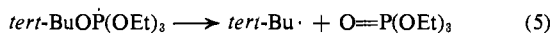
[log k (M^{-1} sec^{-1}) = 10.3 − 7.5/2.303RT;[14d]

$$13.0 - 10.3/2.303RT]^{14b}$$

$$\text{tert-BuOP(OEt)Et}_2 \longrightarrow \text{tert-BuOP(OEt)Et} + \text{Et·} \quad (6)$$

[log k (M^{-1} sec^{-1}) = 10.91 − 8.16/2.303RT][13]

Also clearly shown in Figure 1 is the fact that with RO·, $\Delta H_r°$ for displacement, estimated from $\bar{D}_{PX_3}$ and

(15) (a) W. G. Bentrude and R. A. Wielesek, *J. Amer. Chem. Soc.*, **91**, 2406 (1969); (b) W. G. Bentrude and T. B. Min, *ibid.*, **94**, 1025 (1972).
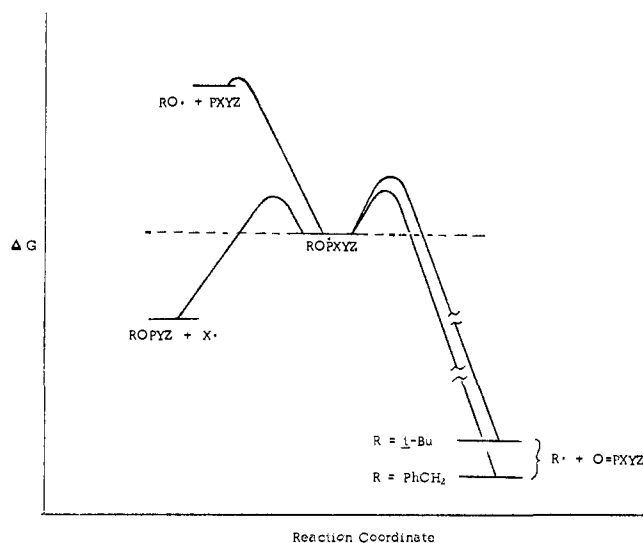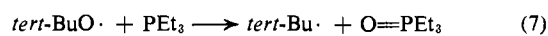(16) W. G. Bentrude, J.-J. L. Fu, and P. E. Rogers, *ibid.*, in press.

Figure 1. Free energy diagram for the reaction of RO· with PXYZ.

$\bar{D}_{P(OR)_3}$, is *always* more favorable than $\Delta H_r°$ oxidation; e.g., for reaction 4 above, $\Delta H_r°$ can be calculated to be about −22 kcal/mol (62 − 84 = −22, see Table IV). For oxidation (eq 7) $D_{P=O}$ for *n*-Bu₃PO is 137 kcal/

$$\text{tert-BuO·} + \text{PEt}_3 \longrightarrow \text{tert-Bu·} + \text{O=PEt}_3 \quad (7)$$

$$(\Delta H = -46 \text{ kcal/mol})$$

mol[17] and D_{C-O} for the process *tert*-BuO· → *tert*-Bu· + O is 91 kcal/mol[18] giving $\Delta H_r°$ for the overall reaction

(17) S. B. Hartley, W. S. Holmes, J. K. Jacques, M. F. Mole, and J. C. McCoubrey, *Quart. Rev., Chem. Soc.*, **17**, 204 (1963).
(18) Calculated from $\Delta H_f°$(298°, g) data[19] for *tert*-BuO·, *tert*-Bu, and O.
(19) J. A. Kerr, *Chem. Rev.*, **66**, 465 (1966).

Table IV. Average Bond Strengths for PX_3 and Bond Dissociation Energies for X_2PPX_2[a]

Compd	$\Delta H_f°(298°, \text{g})$, kcal/mol	Ref	Radical or atom	$\Delta H_f°(298°, \text{g})$, kcal/mol	Ref	Bond	$\bar{D}_{PX_3}$, kcal/mol	D_{PX_3}, kcal/mol
Me_3P	-22.5	n	$Me\cdot$	34.0	o	P–Me	67	
Et_3P	-32.8^c	c	$Et\cdot$	25.7	o	P–Et	62	
	-11.8^d	d	$Et\cdot$	25.7	o	P–Et	55	
Ph_3P	78.5	n	$Ph\cdot$	78.5	j	P–Ph	77	
$(MeO)_3P$	-168.3	n	$MeO\cdot$	2	o	P–OMe	83	
$(EtO)_3P$	-195.9	n	$EtO\cdot$	-6.7	o	P–OEt	84	
$(i\text{-PrO})_3P$	-223.3	n	$i\text{-PrO}\cdot$	-15	o	P–OPr-i	85	
$(Me_2N)_3P$	-45.0	k	$Me_2N\cdot$	29.3	o	P–N	69	
$(Et_2N)_3P$	-52.3	l	$Et_2N\cdot$	17	m	P–N	59	
PCl_3	-68.6	b	$Cl\cdot$	29.1	b	P–Cl	77	
H_2PPH_2	5.0	b	$H_2P\cdot$	25.9^e	f	P–P		47^i
I_2PPI_2	-9.8	h	$I_2P\cdot$	26.0^g		P–P		62^i

[a] $\Delta H_f°$ values are relative to white phosphorus as standard state [$\Delta H_f°(298, \text{g}) = 75.2 \text{ kcal/mol}^b$]. [b] D. D. Wagman, W. H. Evans, V. B. Parker, I. Halow, S. M. Bailey, and R. H. Schumm, National Bureau of Standards Technical Note 270-3, U. S. Government Printing Office, Washington, D. C., 1968. [c] Calculated by H. A. Skinner in *Advan. Organometal. Chem.*, **2**, 49 (1964), from combustion heat data of W. F. Lautsch, P. Erzberger, and A. Trober, *Wiss. Z. Tech. Hochsch. Chem. Leuna-Merseburg*, **1**, 31 (1958). [d] Calculated by authors in ref 21 from the combustion heat data of Lautsch, *et al.* (see footnote c above). Value of $\Delta H_f°$ depends on products assumed. A recent kinetic study, K. W. Egger and T. L. James, *Trans. Faraday Soc.*, **66**, 2560 (1970), lends support to the higher value. [e] Assuming that the value of 30.1 kcal/mol given in footnote f is for red phosphorus reference state. [f] "JANAF Thermochemical Tables," The Dow Chemical Co. [g] Using $\Delta H_f°(298°, \text{g})(I_3P) = 1.4^h$ and $\bar{D}_{PI_3} = 50.2 \text{ kcal/mol}.^h$ [h] A. Finch, P. J. Gardner, and K. K. Sen Gupta, *J. Chem. Soc. A*, 2958 (1969); A. Finch, P. J. Gardner, and A. Hameed, *J. Inorg. Nucl. Chem.*, **32**, 2869 (1970). [i] By mass spectrometry D_{PP} values for H_2PPH_2 (61.2 kcal/mol: T. McAllister and F. P. Lossing, *J. Phys. Chem.*, **73**, 2996 (1969)), Cl_2PPCl_2 (58 kcal/mol: A. A. Sandoval, H. C. Moser, and R. W. Kiser, *ibid.*, **67**, 124 (1963)), and I_2PPI_2 (73 kcal/mol: A. Finch, A. Hameed, P. J. Gardner, and N. Paul, *J. Chem. Soc. D*, 391 (1969)) have been estimated. [j] S. W. Benson and E. Whittle, private communication. See A. S. Rodgers, D. M. Golden, and S. W. Benson, *J. Amer. Chem. Soc.*, **89**, 4578 (1967), for a slightly older value. [k] S. B. Hartley, unpublished results quoted in ref 17. [l] C. T. Mortimer, *Pure Appl. Chem.*, **2**, 71 (1961). [m] Calculated from $\Delta H_f°$ (298°, g) for Et_2NH of -17 kcal/mol[21] and the assumption that the bond dissociation energy for Et_2NH equals that for Me_2NH (86 kcal/mol).[19] [n] J. D. Cox and G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds," Academic Press, New York, N. Y., 1970. [o] J. A. Kerr, *Chem. Rev.*, **66**, 465 (1966).

of -46 kcal/mol. For $(RO)_3PO$, D_{PO} is 148 kcal/mol.[20] Thus, for reaction 3, overall $\Delta H_r°$ is about -57 kcal/mol.

Inspection of the *tert*-BuO· reactions in Tables I and III shows that either process, α or β scission, may be the exclusive one, or both may occur depending on the nature of the leaving radical, X·. The last column of the tables lists the average bond strength (and in a few cases the bond dissociation energy) for the corresponding PX_3 compound as an estimate of the strength of the P–X bond which could potentially be cleaved by displacement. Except as noted, these numbers are those which appear in Table IV and were calculated using the $\Delta H_r°$ data also listed therein. With the notable exception of cases 9 and 11 of Table III, it can be seen that if for one of the substituents (X, Y, or Z) $\bar{D}_{PX_3}$ is less than about 75 kcal/mol, α scission predominates; but if $\bar{D}_{PX_3}$ is greater than 75 kcal/mol, the almost exclusive process is β scission (oxidation). This is clearly demonstrated by comparison of cases 1–5 of Table I and cases 3–10 and 12–15 of Table III. The Cl substituent (Table I, case 6) seems to be borderline [$\bar{D}_{PX_3} = 77$ kcal/mol].

The exceptions to the above generalizations deserve further comment. The formation of some oxide at 130° from n-Bu_3P (case 9, Table III) and not with Et_3P at low temperatures is readily explained if E_a for oxidation (presumably β scission) is greater than that for displacement. The oxide formation on reaction with n-PrP-MePh (case 11, Table III) also appears to be anomalous since the n-Pr or Me substituent would be expected to be displaced preferentially (note cases 2, 3, and 4, Table III). We have suggested elsewhere[16] that phenyl substituents

(20) Calculated from $\Delta H_f°(298°, \text{g})$ data for $(EtO)_3P$,[21] $(EtO)_3PO$,[21] and O.[19]

(21) J. D. Cox and G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds," Academic Press, New York, N. Y., 1970.

may enhance the overall reactivity of trivalent phosphorus compounds toward certain radicals (alkyls, *e.g.*) by reducing E_a for β scission. Reduction in E_a for β scission relative to that for α scission obviously would explain the result with n-PrPMePh.

Also noteworthy is case 8, Table I. Some time ago[22] we suggested that the formation of polymers in the reaction of *tert*-BuO· with $PhOP(OCH_2)_2$ could be the result of P–O ring scission induced by ring strain and subsequent attack by $PhOPOCH_2CH_2O\cdot$ on another PhO-$P(OCH_2)_2$, etc. The high yield of oxidation product in case 8, Table I, leads us to propose, however, that the polymer formation in the earlier study more likely was catalyzed by phenol formed in the reaction.

Further inspection of Table I shows that with Ph-$CH_2O\cdot$ (cases 10–15) β scission becomes more competitive with α scission so that whereas *tert*-BuO· gave very largely displacement, $PhCH_2O\cdot$ yields both oxidation and displacement products. Furthermore, within a series of $RP(OEt)_2$ (cases 10–13), the apparent α scission/β scission ratio increases somewhat with increasing stability of the radical R being displaced.

The results with $PhCH_2O\cdot$ can be interpreted in light of the above effects of P–X bond strength as follows. The β-scission process (structure **2**) requires a relatively

β scission, α scission **2** $\quad$ β scission, α scission **3**
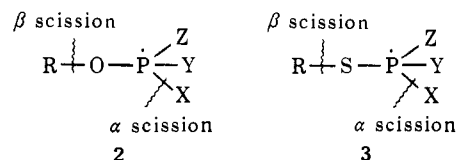
strong C–O bond to be cleaved. This is accompanied by orbital rehybridization and P=O $p\pi$–$d\pi$ bond formation. Apparently, a major portion of the P=O

(22) W. G. Bentrude, *Tetrahedron Lett.*, 3543 (1965).

bond energy which makes β scission the thermodynamically more favorable of the two exothermic processes depicted by Figure 1 is not available to the β-scission transition state; thus, α scission predominates with *tert*-BuO· as reactant and $\bar{D}_{PX_3} < 75$ kcal/mol. Weakening the C–O bond to be cleaved by replacing *tert*-BuO by PhCH₂O lowers the $\Delta G^{\ddagger}$ for β scission (Figure 1) enough for it to compete with α scission. Increasing the stability of R· appears to lower $\Delta G^{\ddagger}$ (α scission) and the α scission/β scission ratio increases (cases 10–13). These and the other results discussed above lead us to conclude that *the competitions between α and β scission are determined primarily by variations in the relative strengths of the C–O and P–X bonds.*

When the reactant radical is RS· rather than RO· (structure **3**), one observes that with all but three rather weak P–X bonds, P–*tert*-Bu, P–CH₂Ph, and P–PEt₂ (cases 3–6, Table II, and case 21, Table III), oxidation is the exclusive process. Displacement is not found even with X = PhO. Oxidation is again quite probably the thermodynamically favored alternative. *E.g.,* one can estimate from $\Delta H_r°(298°, g)$ for RS· → R· + S (for R = *tert*-Bu, 63 kcal/mol)[23] and $\Delta H_r°$ (298°, g) for the process S + P(OEt)₃ → SP(OEt)₃ (91 kcal/mol)[17] that $\Delta H_r°$ for the overall reaction 8 is

$$\text{*tert*-BuS· + P(OEt)₃} \longrightarrow \text{*tert*-Bu· + S=P(OEt)₃} \qquad (8)$$
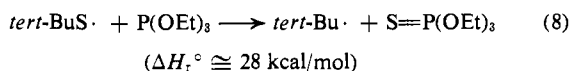
$$(\Delta H_r° \cong 28 \text{ kcal/mol})$$

28 kcal/mol. We are not aware of a $\bar{D}_{P–S}$ value for P(SR)₃, but it is assuredly much less than $\bar{D}_{P–O}$ in P(OR)₃, and $\Delta H_r°$ for displacement by RS· may well be endothermic for many X substituents.

As with reactions of RO· with PXYZ, it is not certain that phosphoranyl radicals are intermediates in all reactions of RS· with PXYZ. The esr spectrum of a species believed to be MeSP(OEt)₃ [a_P = 748.1 G, g = 2.008] has recently been reported.[24] With *tert*-BuS· rather than MeS·, no such intermediate could be found. The latter result is consistent with an intermediate of short lifetime or a mechanistic transition to a concerted sulfur transfer. Regardless, it can be concluded that in analogy to the RO· reactions relative amounts of sulfur transfer and displacement depend *primarily* on the relative strengths of the C–S and P–X bonds in **3**. Only when $D_{P–X}$ is of the order 50–60 kcal/mol is any displacement noted (Table II, cases 3–6, Table III, case 15). The relative amounts of the two scission processes in reaction with PhCH₂P(OEt)₂ vary for the series *i*-PrS·, *tert*-BuS·, and *p*-CH₃C₆H₄CH₂S· in the order expected from R–S bond strengths differences predicted by consideration of the relative stabilities of the radicals (R) *i*-Pr·, *tert*-Bu·, and *p*-CH₃C₆H₄CH₂·. Also, displacement occurs with *tert*-BuP(OEt)₂ when *i*-PrS· is the reactant but not with *tert*-BuS·.

It should be strongly emphasized that the interpretation of the oxidation–displacement trends noted in Tables I, II, and III in terms of the effects of relative bond energies (radical stabilities) on activation free energies for α and β scission may well turn out to be somewhat oversimplified. First of all, entropy effects have been ignored. Secondly, in truly pentacovalent

systems, displacements are stereospecific in nature, generally being subject to the restriction that groups enter and leave *via* axial positions in the trigonal bipyramidal structure.[25] Earlier work[15b] has shown clearly that alkoxy groups are not introduced in a configurationally random way into the intermediate (RO)₄P· on reaction of RO· with (RO)₃P. Esr shows[12,13] the alkyl groups in R₂P(OR)₂ to be configurationally equivalent (presumably equatorial). If the most stable phosphoranyl radical from reaction of RO· with R′P(OEt)₂, *e.g.,* were to be formed fastest, and it is assumed that radicals enter and leave the trigonal bipyramid axially, then the initially formed intermediate would be **4**. This stability prediction is
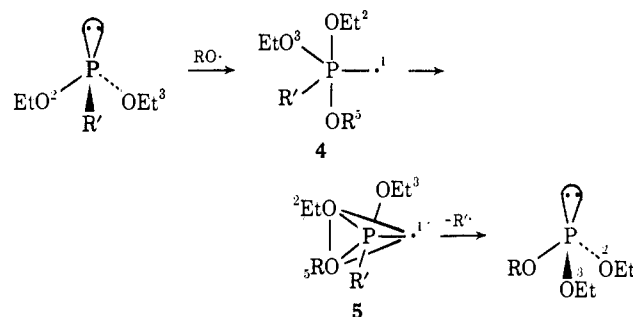
based on the polarity rule[25,26] applicable to pentacovalent systems which predicts that electronegative substituents (*e.g.,* alkoxy) will have an axial preference while more electropositive ones will be equatorial (alkyl groups, odd electron). In **4**, however, R′ is not in position to leave axially. Conversion of **4** to **5** by a Berry pseudorotation or its permutational equivalent[27] would place R′ in position to exit. By the polarity rules, **5** would be predicted to be of higher energy than **4**. Depending on its rate *step* **4** → **5** *could become rate-limiting so far as displacement of R′· is concerned* as has been suggested by Davies, *et al.*[13] The activation energies for pseudorotations which place a single alkyl group in the axial rather than equatorial position in pentacovalent phosphorus systems are of the order of 12–17 kcal/mol.[28] Substituent interchange processes have been inferred from temperature effects on esr spectra of F₄P·[9b,29] and *tert*-BuOPH₃.[30] Studies designed to determine the role of substituent electronegativities and interchange processes on the mechanistic details of these oxidation and displacement reactions are in progress.

A final consideration would be the role of steric effects on the α *vs.* β scission competition. The relatively high proportion of α scission with *tert*-BuP(OEt)₂ (Tables I and II) may reflect relief of steric strain in the intermediate, *e.g.,* ROP(OEt)₂Bu-*tert*. On the other hand, steric interactions of an axial *tert*-butyl in **5** could raise the energy of that intermediate (90° interactions) compared to **4** and thereby slow the rate of α scission. Steric effects in these systems also deserve further study.

(23) H. Mackle, *Tetrahedron*, 19, 1159 (1963).

(24) A. G. Davies, D. Griller, and B. P. Roberts, *J. Organometal. Chem.*, 38, C8 (1972).

(25) F. H. Westheimer, *Accounts Chem. Res.*, 1, 70 (1968); K. Mislow, *ibid.*, 3, 321 (1970).

(26) E. L. Muetterties, *ibid.*, 3, 266 (1970).

(27) See, *e.g.,* I. Ugi, D. Marquarding, H. Klusacek, and P. Gillespie, *ibid.*, 4, 288 (1971).

(28) D. Gorenstein, *J. Amer. Chem. Soc.*, 92, 644 (1970); D. Houlla, R. Wolf, D. Gagnaire, and J. B. Robert, *Chem. Commun.*, 443 (1969).

(29) P. W. Atkins, *Mol. Phys.*, 13, 37 (1967).

(30) P. J. Krusic, private communication.

Experimental Section

Spectra were determined using the following instruments: nmr, Varian A-60 and A-56/60; ir, Beckmann IR-5A; mass spectra, Perkin-Elmer 270 equipped with a gas chromatograph inlet system and A.E.I. MS-30 (high resolution mass spectra). Analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. Boiling points are uncorrected.

The known compounds n-Bu$_2$NP(OEt)$_2$,[31] ClP(OEt)$_2$,[32] AcOP-(OEt)$_2$,[33] MeOP(OCH$_2$)$_2$,[34] EtP(OEt)$_2$,[35] PhCH$_2$P(OEt)$_2$,[35] and MeP(OEt)$_2$[36] were all synthesized according to literature procedures and were purified by vacuum distillation. These and the trivalent phosphorus compounds described below were converted routinely to the corresponding oxides by addition of a saturated CH$_2$Cl$_2$ solution of N$_2$O$_4$ to the trivalent phosphorus compound at 0° in CH$_2$Cl$_2$. The corresponding sulfides, with the exception of (EtO)$_2$P(S)Cl, were synthesized by addition of sulfur to the trivalent phosphorus compound neat or in solution depending on reactivity. Sulfides and oxides were purified by vacuum distillation. The benzyl[36] and tert-butyl[7] hyponitrite were synthesized according to procedures described previously in the literature.

Ethyl Phosphorochloridothioate. A solution of sulfur (3.2 g, 0.10 mol), aluminum chloride (13 g, 0.10 mol), and 200 ml of benzene was stirred vigorously with a mechanical stirrer under a cover of nitrogen at 0°. Diethyl phosphorochloridite (15.6 g, 0.10 mol) in 50 ml of benzene was added over a period of 30 min. The reaction mixture was then warmed to 80° and refluxed for 14 hr. On cooling to room temperature, the solution was filtered through glass wool, and the benzene was removed at aspirator pressure. The residue was distilled to give 15 g (80%) of the chloridothioate: bp 71° (5.0 mm) [lit.[37] bp 71.5–72° (7.0 mm)]; ir identical with a published[38] spectrum.

Diethyl Phenyl Phosphite.[39] A solution of phosphorus trichloride (50 g, 0.364 mol) in 500 ml of anhydrous ether was stirred mechanically under a cover of nitrogen at −10°. This temperature was maintained during the course of all additions beginning with that of triethylamine (37.1 g, 0.366 mol) which was followed by the slow addition of a solution of phenol (34.3 g, 0.364 mol) in 200 ml of ether over a period of 2 hr. At this point another 73.8 g of triethylamine (0.728 mol) was added followed by the slow addition of ethanol (33.5 g, 0.728 mol) in 50 ml of ether. The reaction was then warmed and allowed to reflux for 1 hr. The amine hydrochloride was removed by filtration through a glass wool pad under a cover of nitrogen and the solvent was removed at reduced pressure. Distillation of the residue yielded 41 g (53%) of the phosphite: bp 181–183° (17 mm) [lit.[39] bp 111–112° (11 mm)]; ir (film) 2984, 2920, 1595, 1495, 1210, 1050, 1014, 946, 914, 857, 780–750, 710, 690 cm^{-1}; nmr (CDCl$_3$) δ 7.12 (m, 5, aryl), 3.98 (quint, 4, J_{HH} = 7.2 Hz, J_{HP} = 7.2 Hz, CH$_3$CH$_2$O), 1.27 (t, 6, J_{HH} = 7.2 Hz, CH$_3$CH$_2$O).

Benzyl Diethyl Phosphite.[40] A procedure identical with that used to prepare diethyl phenyl phosphite was followed. Purification by vacuum distillation yielded the benzyl phosphite in 42% yield: bp 78° (0.025 mm) [lit.[40] bp 85–88° (1 mm)]; ir (film) 3075, 2985, 2940, 2890, 1505, 1460, 1395, 1208, 1180, 1101, 1090–980, 980–870, 834, 820–720, 695 cm^{-1}; nmr (CDCl$_3$) δ 7.26 (s, 5, aryl), 4.81 (d, 2, J_{HP} = 7.8 Hz, PhCH$_2$O), 3.82 (quint, 4, J_{HP} = 7.2 Hz, J_{HH} = 7.2 Hz, CH$_3$CH$_2$O), 1.18 (t, 6, J_{HH} = 7.2 Hz, CH$_3$CH$_2$O).

Anal. (as phosphate) Calcd for C$_{11}$H$_{17}$O$_4$P: C, 54.09; H, 7.02; P, 12.68. Found: C, 53.99; H, 7.11; P, 12.69.

Diethyl tert-Butyl Phosphite. A solution of diethyl phosphoro-

(31) A. I. Razumov, *Tr. Kazan. Khim. Tekhnol. Inst.*, **23**, 201 (1957); *Chem. Abstr.*, **52**, 9947e (1958).

(32) H. G. Cook, J. P. Ilett, B. C. Saunders, G. J. Stacey, H. G. Watson, I. G. E. Wilding, and S. J. Woodcock, *J. Chem. Soc.*, 2921 (1949).

(33) M. I. Kabachnik, T. A. Mastryukova, and A. E. Shilov, *Zh. Obshch. Khim.*, **33**, 320 (1963).

(34) B. A. Arbuzov, M. K. Saikima, and V. M. Zoroastrova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1046 (1957).

(35) M. Sander, *Chem. Ber.*, **93**, 1220 (1960).

(36) F. W. Hoffmann and T. R. Moore, *J. Amer. Chem. Soc.*, **80**, 1150 (1958).

(37) J. H. Fletcher, J. C. Hamilton, I. Hechenbleikner, E. I. Hoegberg, B. J. Sertl, and J. T. Cassaday, *J. Amer. Chem. Soc.*, **70**, 3943 (1948).

(38) R. A. McIvor, C. A. Grant, and C. E. Hubley, *Can. J. Chem.*, **34**, 1611 (1956).

(39) G. Kamai and F. M. Kharrasova, *Tr. Kazan. Khim. Tekhnol. Inst.*, **23**, 122 (1957); *Chem. Abstr.*, **52**, 9980i (1958).

(40) F. W. Hoffmann, R. J. Ess, and R. P. Usinger, *J. Amer. Chem. Soc.*, **78**, 5817 (1956).

chloridite (30.0 g, 0.20 mol) in 1 l. of ether was maintained at −40° and stirred mechanically under a cover of nitrogen. Triethylamine (20.2 g, 0.20 mol) was added over a period of several minutes followed by the dropwise addition of 14.8 g of tert-butyl alcohol (0.20 mol) over a span of 2 hr. Following this addition the reaction was allowed to warm to room temperature and was stirred for 5 hr. The insoluble salts were filtered off under a cover of nitrogen and the ether was removed at reduced pressure. The residue was distilled to give 22.1 g (59%) of the desired phosphite: bp 56° (9 mm); ir (film) 2985, 2930, 1379, 1320, 1260, 1027, 1000–950, 950–900, 810, 780–720, 700 cm^{-1}; nmr (CDCl$_3$) δ 3.84 (quint, 4, J_{HP} = 7.2 Hz, J_{HH} = 7.2 Hz, CH$_3$CH$_2$O), 1.42 (s, 9, (CH$_3$)$_3$C–O), 1.24 (t, 6, J_{HH} = 7.2 Hz, CH$_3$CH$_2$O). The elemental composition of this compound was established by high resolution mass spectrometry (A.E.I. MS-30, 70 eV): M$^+$, 194.1056 (calcd for C$_6$H$_{19}$O$_3$P, 194.1072).

Diethyl tert-Butylphosphonite. Following the general procedure outlined by Kabachnik and Tsvetkov,[41] tert-butylmagnesium chloride from magnesium (10 g, 0.41 mol) and tert-butyl chloride (37 g, 0.40 mol) in 200 ml of ether were added slowly to a solution of diethyl phosphorochloridite (46.2 g, 0.295 mol) in 300 ml of ether at −65° under a cover of nitrogen. The well-stirred mixture was then allowed to warm to room temperature overnight. The inorganic salts were removed by filtration through glass wool under nitrogen, and the solvent was removed at reduced pressure. Distillation yielded 31.6 g (60%) of the diethyl tert-butylphosphonite: bp 50–53° (13 mm); ir (film) 2950, 1488, 1390, 1380, 1103, 1068, 1042, 912, 813, 734 cm^{-1}; nmr (CDCl$_3$) δ 0.93 (d, 9, J_{HP} = 13 Hz, (CH$_3$)$_3$-CP), 1.23 (t, 6, J_{HH} = 7 Hz, CH$_3$CH$_2$OP), 3.90 (m, 4, J_{HP} = 8.5 Hz, J_{HH} = 7 Hz, CH$_3$CH$_2$OP); mass spectrum (70 eV) m/e (rel intensity) 178 (21), 133 (15), 121 (80), 94 (100), 65 (68), 88 (20), 57 (31), 41 (22), 29 (19). The diethyl tert-butylphosphonite was converted to diethyl tert-butylphosphonothionate: bp 68° (3.2 mm); ir (film) 2950, 1488, 1480, 1392, 1330, 1159, 1040, 945, 825, 770, 692 cm^{-1}; nmr (CDCl$_3$) δ 4.10 (m, 4, CH$_3$CH$_2$OP), 1.28 (t, 6, J_{HH} = 7 Hz, CH$_3$CH$_2$OP), 1.18 (d, 9, J_{HP} = 18 Hz, (CH$_3$)$_3$CP).

Anal. Calcd for C$_8$H$_{19}$O$_2$PS: C, 45.70; H, 9.03; P, 14.97. Found: C, 45.88; H, 8.96; P, 14.77.

Literature procedures[42] gave O,O-diethyl S-(tert-butyl)phosphorodithioate and O,O-diethyl S-(isopropyl)phosphorodithioate. The new compound O,O-diethyl S-(p-methylbenzyl)phosphorodithioate was prepared in 48% yield by the reaction of the sodium salt of ethyl phosphorodithioate with p-methylbenzyl bromide in methanol at 50°: bp 132–134° (0.07 mm); ir (film) 2970, 1505, 1440, 1380, 1160, 1080–990, 990–910, 850–760, 710–640 cm^{-1}; nmr (CDCl$_3$) δ 7.35–6.95 (m, 4, aryl), 4.4–3.8 (m, 6, OCH$_2$CH$_3$, CH$_2$S), 2.32 (s, 3, ArCH$_3$), 1.35 (t, 6, J = 7 Hz, OCH$_2$CH$_3$).

Anal. Calcd for C$_{12}$H$_{19}$O$_2$PS$_2$: C, 49.63; H, 6.59. Found: C, 49.52; H, 6.54.

Reactions of tert-BuO· and BzO· with PXYZ. The reactions of these alkoxy radicals were carried out in Pyrex tubes (120 mm × 9 mm) which had been sealed with serum stoppers and flushed with nitrogen. When di-tert-butyl hyponitrite was used, the phosphorus compound, hyponitrite, and solvent were first added. The tube was degassed with three freeze–thaw cycles at 10^{-5} mm and then sealed under vacuum. In the reactions of benzyloxy radicals, the phosphorus compound and solvent were added and allowed to come to the desired temperature before a solution of the dibenzyl hyponitrite was added. In both cases, the reactions were run for 10 half-lives of the radical precursor before being cooled to room temperature, opened under a cover of nitrogen, and analyzed by glpc. Reactions of diethyl methylphosphonite were analyzed on a 6 ft × 0.25 in. column containing a (2:1) mixture of 20% SE-30 and 20% DEGS on 60–80 Chromosorb W, reg. Reactions of diethyl ethylphosphonite, diethyl benzylphosphonite, and diethyl phenyl phosphite were analyzed on a 4.5 ft × 0.25 in. column of 20% Carbowax 20M on 60–80 Chromosorb W, reg. All other reactions of alkoxy radicals were analyzed on 6 ft × 0.25 in. 20% SE-30 on 60–80 Chromosorb W, regular. All quantitative measurements were made using appropriate internal standards and sensitivity corrections.

Reactions of RS· with PXYZ. Pyrex tubes (120 mm × 9 mm) were sealed with a serum stopper and flushed with nitrogen and the phosphorus compound, mercaptan, solvent, and 0.005 equiv of

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AIBN were then added. In general, the tubes were degassed at 10^{-5}–10^{-6} mm with three successive freeze–thaw cycles before sealing under vacuum. In several cases the reactions were run under a cover of nitrogen, warming the reaction mixtures to the temperature under study before the addition of the initiator. After 2 hr the reaction mixtures were cooled to room temperature, opened under a cover of nitrogen, and sealed with a serum stopper before being analyzed by glpc. Analyses were performed on aluminum 4–7 ft $\times$ 0.25 in. 20% SE-30 on 60–80 Chromosorb W, reg columns.

Quantitative measurements were made with the use of appropriate internal standards and sensitivity corrections.

Catalytic Action of Polyelectrolytes on the Alkaline Fading Reactions of Triphenylmethane Dyes[1]

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Abstract: The alkaline fading reactions of crystal violet (CV), ethyl violet (EV), malachite green (MG), and brilliant green (BG) in aqueous solutions (reactions between oppositely charged ionic species) were studied in the presence of cationic and anionic polyelectrolytes and surfactants. The polymer catalysts examined are poly-(4-vinylpyridine) quaternized with alkyl halide (C_nPVP) [alkyl = ethyl ($n = 2$), n-propyl (3), n-butyl (4), and cetyl 16)] and with benzyl halide (BzPVP), copolymer of diethyldiallylammonium chloride and sulfur dioxide (DECS), sodium poly(ethylene sulfonate) (NaPES), sodium poly(styrene sulfonate) (NaPSS), sodium polyacrylate (NaPAA), and NaDNA. Surfactants used are cetyltrimethylammonium bromide and sodium lauryl sulfate. The fading reactions of CV, EV, MG, and BG are *accelerated* by the cationic polyelectrolytes having hydrophobic groups. The largest acceleration factor observed is $\sim 10^2$ for the EV–CTABr system, and the strength of the acceleration is in the order: C_2PVP $< C_3$PVP $< C_4$PVP $<$ BzPVP $< C_{16}$BzPVP. By the addition of anionic polyelectrolyte, on the other hand, the fading reaction is *retarded* with the largest deceleration factor of 10^4 for the EV–NaPSS system, and the order of the retarding efficiency is NaPES $\sim$ NaPAA $\ll$ NaDNA $<$ NaPSS. The acceleration and deceleration factors caused by the catalysts are largest for EV and smallest for MG with the order: MG $<$ BG $<$ CV $<$ EV. These results suggest the important contribution of the hydrophobic interactions between the dye and the polymer catalyst. The acceleration by the hydrophobic cationic polymer is due to the enthalpic loss, whereas the deceleration by the hydrophobic anionic polymer is due to a decrease of entropy. The fading of phenolphthalein (PP) (reaction between ionic species with charges of the same sign) is not influenced by anionic polymers, whereas it is accelerated by cationic polymers having small hydrophobic groups and decelerated strongly by highly hydrophobic cationic polymers.

R ecently, there appeared a large number of publications dealing with organic and inorganic reactions in the presence of polyelectrolytes.[2] In our laboratory, catalytic action of polyelectrolytes on interionic reactions has been studied in order to understand the nonspecific, general aspect of the polymer catalyses.[3–9] Other types of interactions, such as hydrophobic, hydrogen-bonding, and charge-transfer interactions between ionic reactant and catalyst, how-

ever, are easily understood to be also important and can be even more so under some circumstances than electrostatic ones. The purpose of the present work is mainly to discuss the comparative strength of contributions of various interactions between a substrate and a polymer catalyst. The relative strength of the hydrophobic interactions in comparison with the electrostatic ones will be considered. The principal contribution of the hydrophobic interactions between substrate and catalyst in interionic reactions was demonstrated first by Grunwald, *et al.*,[10–12] and quite recently by Cordes, *et al.*,[13] for alkaline fading reactions of triphenylmethane dyes in the presence of detergents. A similar conclusion was reached by Sakurada for a series of hydrolysis reactions of various esters in the presence of polysulfonic acid.[14] The triphenylmethane dye is a hydrophobic ionic substrate, and the fading reactions of the dye with hydroxide ion have been

(1) Presented at the 20th Symposium of Polymer Science, Tokyo, Japan, Nov 1971. The term "catalytic action of polyelectrolyte" is used throughout the present paper in the customary fashion. However, we do not imply that the polyelectrolytes are really catalysts as defined earlier by W. Ostwald, *Phys. Z.*, **3**, 313 (1902).

(2) See, for example, H. Morawetz, *Advan. Catal. Relat. Subj.*, **20**, 341 (1969); H. Morawetz, *Accounts Chem. Res.*, **3**, 354 (1970); N. Ise, *Advan. Polym. Sci.*, **7**, 536 (1971). Similar studies have been reported with micelles instead of polyelectrolytes. See, for example, E. H. Cordes and R. B. Dunlop, *Accounts Chem. Res.*, **2**, 329 (1969); E. J. Fendler and J. H. Fendler, *Advan. Phys. Org. Chem.*, **8**, 271 (1970).

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