Table I. Hyperfine Coupling Constants of Radicals Derived from Trialkoxyboranes[a]

Trialkoxyborane	Radical	Temp, °C	Coupling constants, G a_α	a_B	a_β	a_γ
Trimethoxy	$(CH_3O)_2BO\dot{C}H_2$	−34	20.14	0.35		
Triethoxy	$(C_2H_5O)_2BO\dot{C}HCH_3$	−54	18.55	0.66	23.52	
Tri-*n*-propoxy	$(C_3H_7O)_2BO\dot{C}HCH_2CH_3$	−48	18.5	0.4	23.4	0.4
Triisopropoxy	$(C_3H_7O)_2BO\dot{C}(CH_3)_2$[b]	−55		*c*	19.5	

[a] From photolysis of solutions containing 10% (v/v) di-*t*-butyl peroxide at 2500–3500 A. [b] In addition to a second paramagnetic species with hfs a_H = 20.70 G (quintet or septet) and a_B = 5.45 G. [c] Not determined due to complications from second-order effects.

4, differs from the molecular mechanism postulated earlier for the autoxidation of these compounds.[15,16]

The behavior of *trialkoxy*boranes toward *t*-butoxy radicals is entirely different from the *trialkyl*boranes discussed above. Thus, the esr spectrum obtained from the reaction of triethoxyboron and *t*-butoxy radical is shown in Figure 3, and there is no evidence for the formation of ethyl radicals. The radical species is identified as the radical IV, which is formed from triethoxyboron by abstraction of one of the methylene hydrogens by *t*-butoxy radical (eq 7). In addition to the doublet and quartet splittings due to the α and β

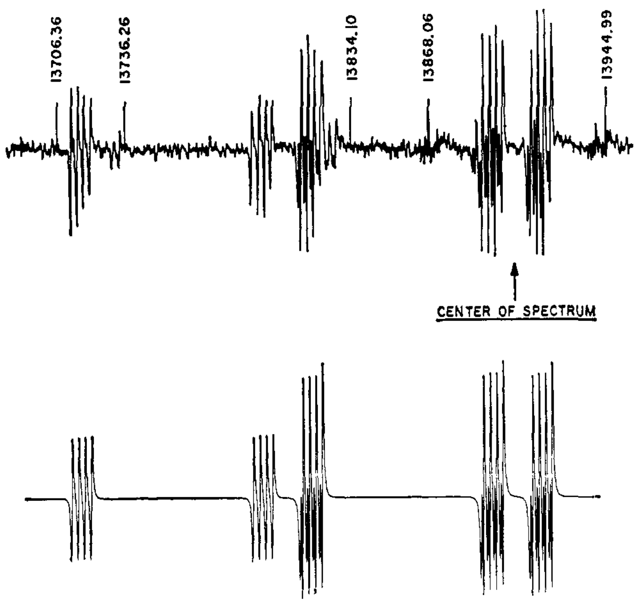

Figure 3. Experimental and calculated esr spectra of $(CH_3CH_2O)_2BO\dot{C}HCH_3$ from triethoxyboron at −54°. Part of the fine structure is due to second-order effects.

$$(CH_3CH_2O)_2BOCH_2CH_3 + \cdot OBu\text{-}t \longrightarrow (CH_3CH_2O)_2BO\dot{C}HCH_3 + t\text{-BuOH} \quad (7)$$

IV

protons, the esr spectrum shows a further quartet splitting due to the ^{11}B nucleus. The ^{11}B coupling constant shows a pronounced temperature variation of approximately 0.01 G/degree between −20 and −100°.

A variety of trialkoxyboranes (listed in Table I) also react with *t*-butoxy radicals to generate analogous species by abstraction of the protons α to the ethereal oxygen. The pertinent hyperfine coupling constants for these radicals are also included in Table I.

The abstraction of a hydrogen from trialkoxyboranes (eq 7) rather than a displacement (eq 4) can be, in part, attributed to the activating effect of a neighboring oxygen atom. Similar processes have been observed by esr in reactions of alcohols and ethers with hydroxy and *t*-butoxy radicals.[17]

Acknowledgment. We thank Mr. K. Eaby for technical assistance.

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(15) A. G. Davies, *Progr. Boron Chem.*, **1**, 276 (1964).

(16) (a) The autoxidation of organometallic derivatives of group I and II could also proceed *via* mechanism 3–4. However, these compounds are generally more ionic, and oxidation may occur *via* the carbanion [*cf.* G. A. Russell and A. Bemis, *J. Am. Chem. Soc.*, **88**, 5491 (1966)]. (b) For autoxidation of Grignard reagents, see R. C. Lamb, P. W. Ayers, M. K. Toney, and J. F. Garst, *ibid.*, **88**, 4262 (1966).

(17) (a) W. T. Dixon and R. O. C. Norman, *J. Chem. Soc.*, 3119 (1963); (b) R. Livingston and H. Zeldes, *J. Chem. Phys.*, **44**, 1245 (1966); **45**, 1946 (1966); *J. Am. Chem. Soc.*, **88**, 4333 (1966); (c) J. Q. Adams, *ibid.*, 90, 5363 (1968); (d) P. J. Krusic, to be published.

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The Displacement of Alkyl Groups from Organophosphorus Compounds Studied by Electron Spin Resonance

Sir:

Organophosphorus compounds are involved in a variety of free-radical reactions.[1] Autoxidation generally exhibits radical chain character and as a class of reactions is particularly interesting because of its complexity.[2] Mechanisms involving alkyl, alkylperoxy, and alkoxy radicals as the principal reactive intermediates have been proposed. Alkoxy radicals have been postulated to react with alkylphosphines by either displacement (eq 1) or oxygen-atom transfer (eq 2).[1] Heretofore, no direct evidence has been brought forth to establish any of these homolytic processes.

$$R_3P + \cdot OR' \longrightarrow R_2POR' + R\cdot \quad (1)$$

$$R_3P + \cdot OR' \longrightarrow R_3PO + R'\cdot \quad (2)$$

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(1) (a) C. Walling and M. S. Pearson, *Topics Phosphorus Chem.*, **3**, 1 (1966); (b) J. I. G. Cadogan, *Advan. Free Radical Chem.*, **2**, 203 (1967); (c) A. J. Kirby and S. G. Warren, "The Organic Chemistry of Phosphorus," Elsevier Publishing Co., Amsterdam, 1967, p 158 ff; (d) J. I. G. Cadogan, *Quart. Rev.* (London), **16**, 208 (1962); (e) J. H. Boyer and J. D. Woodyard, *J. Org. Chem.*, **33**, 3329 (1968).

(2) (a) S. A. Buckler, *J. Am. Chem. Soc.*, **84**, 3093 (1962); (b) M. B. Floyd and C. E. Boozer, *ibid.*, **85**, 984 (1963); (c) F. R. Mayo, L. J. Durham, and K. S. Griggs, *ibid.*, **85**, 3156 (1963).

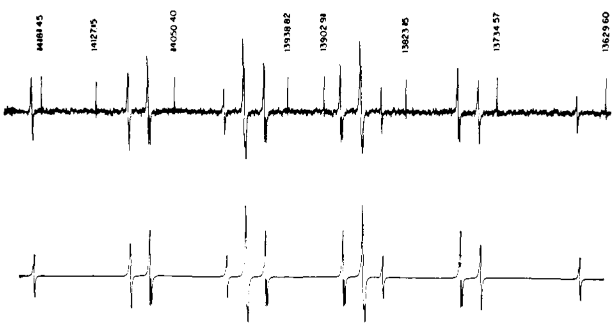


Figure 1. The esr spectrum obtained from the photolysis of a solution of di-*t*-butyl peroxide in triethylphosphine at −90°. The computer-simulated spectrum of ethyl radical including second-order effects is shown below. The proton nmr field markers are in kilocycles per second.

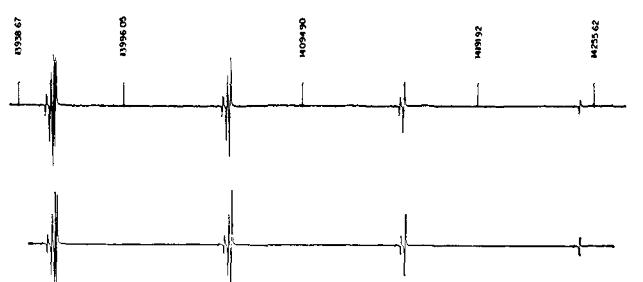


Figure 2. Esr spectrum of *t*-butyl radical from the photolysis of di-*t*-butyl peroxide in triethyl phosphite at −90°. Four of the ten "lines" are shown with resolved second-order structures.

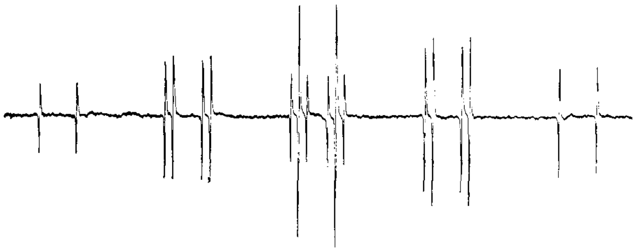


Figure 3. Esr spectrum of allyl radical from the photolysis of di-*t*-butyl peroxide in triallyl phosphite at −70°.

We wish to report an electron spin resonance (esr) study of the transient radical species produced in the reactions between various organophosphorus compounds and alkoxy as well as thiyl radicals.

Previous studies have shown that photolysis of di-*t*-butyl peroxide is well suited for the production of *t*-butoxy radicals for electron spin resonance studies.[3] In the presence of triethylphosphine, we observed an intense and well-resolved esr spectrum of ethyl radical (Figure 1) as the sole paramagnetic species.[4] No esr spectrum was observed in the absence of di-*t*-butyl peroxide or irradiation. Similarly, in the reactions

$$(CH_3CH_2)_3P + (CH_3)_3CO\cdot \longrightarrow (CH_3)_3COP(CH_2CH_3)_2 + CH_3CH_2\cdot \quad (3)$$

between *t*-butoxy radicals and triisobutyl-, triisopropyl-, and tricyclohexylphosphines in cyclopropane solutions, only the esr spectra of isobutyl, isopropyl, and cyclohexyl radicals, respectively, were observed. *t*-Butyl radicals expected from a reaction such as (4) were not

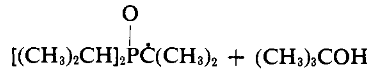
$$(CH_3CH_2)_3P + (CH_3)_3CO\cdot \longrightarrow (CH_3CH_2)_3PO + (CH_3)_3C\cdot \quad (4)$$

detected. They were, however, the only species observed when *t-butylthiyl* radicals generated from the photolysis of di-*t*-butyl disulfide[5] reacted with triisopropylphosphine under the same conditions.

$$[(CH_3)_2CH]_3P + \cdot SC(CH_3)_3 \longrightarrow [(CH_3)_2CH]_3PS + (CH_3)_3C\cdot \quad (5)$$

Trimethylphosphine under equivalent conditions yielded an esr spectrum of methyl radicals, although it was not as intense as those derived from the other alkyl analogs. In addition, a phosphorous-centered radical was observed exhibiting a large phosphorus splitting (a_P = 618 G) and additional fine structure.[6,7]

$$[(CH_3)_2CH]_3PO + \cdot OC(CH_3)_3 \longrightarrow$$



$$[(CH_3)_2CH]_2\overset{\overset{\textstyle O}{|}}{P}\dot{C}(CH_3)_2 + (CH_3)_3COH \quad (6)$$

I

The behavior of trialkyl *phosphites* toward alkoxy radicals is in sharp contrast to that observed with trialkyl*phosphines*. For example, when triethyl phosphite was subjected to *t*-butoxy radicals under the same conditions, the esr spectrum of only the *t*-butyl radical (Figure 2) was detected. Triisopropyl and trimethyl phosphite also yielded only *t*-butyl radical. No paramagnetic species was observed in the absence of di-*t*-butyl peroxide. These esr studies, thus, provide direct and unequivocal evidence for oxygen loss from the *t*-butoxy radical in the presence of trialkyl phosphites. Such an oxygen transfer can occur by reactions postulated earlier on the basis of chemical studies.[8] An analogous

$$(CH_3CH_2O)_3P + (CH_3)_3CO\cdot \longrightarrow (CH_3CH_2O)_3PO + (CH_3)_3C\cdot \quad (7)$$

sulfur atom transfer also occurs, as evidenced by the appearance of only *t*-butyl radicals when triisopropyl phosphite is allowed to react with *t*-butylthiyl radicals.[9]

Triallyl phosphite, on the other hand, reacted with *t*-butoxy radicals by the same method, to give only an intense spectrum of the allyl radical (Figure 3), obviously produced by a process such as (8).

The scission of the phosphorus–oxygen bond is observed when the displaced oxy radical is resonance stabilized. Thus, the esr spectrum of the phenoxy

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[3] P. J. Krusic and J. K. Kochi, *J. Am. Chem. Soc.*, 90, 7155 (1968).

[4] After this work was submitted, Adams and Ingersoll (Abstracts, 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 13, 1969, PETR-002) reported an incorrect assignment for the spectrum of ethyl radical to $(CH_3CH_2)_2P\dot{C}HCH_3$.

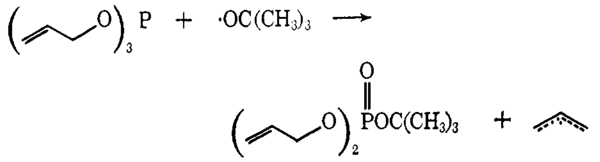
[5] Esr studies of thiyl radicals from the photolysis of alkyl disulfides will be reported.

[6] We assign the spectrum to the radical $(CH_3)_3\dot{P}OC(CH_3)_3$ in which one methyl group is distinct from the other two. Phosphine and methyl- and dimethylphosphine show similar behavior consistent with a trigonal-bipyramidal configuration (P. J. Krusic, W. Mahler, and J. K. Kochi, to be published). Similar structures have been postulated for other phosphorus radicals (P. W. Atkins and M. C. R. Symons, *J. Chem. Soc.*, 4363 (1964); R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **45**, 1845 (1966); G. Kokoszka and F. E. Brinkman, *Chem. Commun.*, 349 (1968).

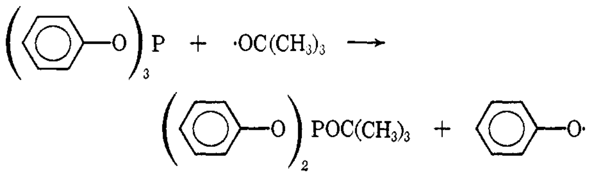
[7] Under reaction conditions trialkylphosphine oxides are not formed from trialkylphosphines and di-*t*-butyl peroxide (*cf.* L. Horner and G. Jurgeleit, *Ann.*, **591**, 138 (1955), and they cannot be precursors for the alkyl radicals. In fact, *t*-butoxy radicals generated photochemically react with triisopropylphosphine oxide by *hydrogen abstraction* to generate radical I (a_{CH_3}(septet) = 23.2, a_P(doublet) = 35.6, a_{CH}(doublet) = 2.4 G).

[8] (a) C. Walling and P. Rabinovitch, *J. Am. Chem. Soc.*, **81**, 1243 (1959); (b) C. Walling and R. Pearson, *ibid.*, **86**, 2262 (1964).

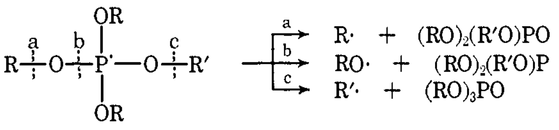
[9] *Cf.* (a) C. Walling, O. H. Basedow, and E. S. Savas, *ibid.*, **82**, 2181 (1960); (b) W. G. Bentrude, J. H. Hargis, and P. E. Rusek, *Chem. Commun.*, 296 (1969).


(8)

radical[10] was obtained when a dilute solution of triphenyl phosphite and di-*t*-butyl peroxide in cyclopropane was irradiated at −85°.[11]

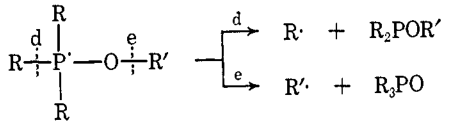

(9)

It is possible to rationalize the multiplicity of behavior of phosphite esters toward alkoxy radicals in the foregoing reactions (eq 7, 8, and 9), by considering a common four-coordinate phosphorus-centered radical intermediate such as II, which fragments to yield the most stable radical (eq 10).[12]


II

(10)

A phosphoranyl radical intermediate III similar to II can also account (eq 11) for the homolytic displacement of alkyl groups from trialkylphosphines by *t*-butoxy radicals (eq 3) and the sulfur-atom transfer from *t*-butylthiyl radicals to trialkylphosphines (eq 5). Except in the case of methylphosphines,[6] however, we have been unable to detect such an intermediate. The lifetimes of these phosphoranyl radicals are too short for detection and are presumably related to the ease with which alkyl radicals are expelled.[13] Finally, it should be added that the homolytic displacement reactions of eq 1 are not limited to phosphines but have been observed also with trialkylarsenic and trialkylantimony compounds. Thus, only the spectrum of ethyl radicals was detected when triethylarsenic and triethylantimony were subjected to *t*-butoxy radicals. The nitrogen analogs, on the other hand, do not generate alkyl radicals under the same conditions.[14, 15]


III

(11)

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[10] The presence of a relatively long-lived radical species giving rise to a broad singlet obscured the spectrum of phenoxy radical (a_0 = 6.78, a_m = 1.90, and a_P = 10.04 G; T = −55°) on prolonged irradiation (*cf.* ref 4). Nmr analysis showed the absence of phenol in the sample prior to irradiation.

[11] Chemical studies lead to the same conclusion [W. G. Bentrude, *Tetrahedron Letters*, 3543 (1965); *J. Am. Chem. Soc.*, **87**, 4062 (1965)].

[12] Recent tracer studies have also pointed strongly to such a phosphoranyl radical intermediate [W. G. Bentrude and R. A. Wielesek, *ibid.*, **91**, 2406 (1969)].

[13] Whether the reaction proceeds by direct displacement [S_H2 mechanism; *cf.* W. A. Pryor, "Free Radicals," McGraw-Hill Book Co., Inc., New York, N. Y., 1966, p 9] or *via* a metastable four-coordinate species at this juncture is a moot point.

[14] For example, triethylamine does not afford ethyl radicals. A paramagnetic species is formed, however, and further studies of amines are in progress.

Acknowledgment. We wish to thank Mr. K. Eaby for technical assistance.

[15] Irradiation of a solid solution of hydrogen peroxide and triethylamine has been reported to form ethyl radicals [V. I. Mal'tsev and A. A. Petrov, *J. Org. Chem., USSR*, **3**, 205 (1967).].

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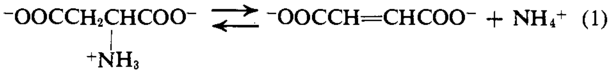
The Kinetics and Mechanism of the Nonenzymatic Reversible Deamination of Aspartic Acid

Sir:

The reversible deamination of aspartic acid, which yields fumaric acid and ammonia, is catalyzed by aspartase, an enzyme which has been isolated from several microorganisms and a few higher plants. This deamination reaction also occurs nonenzymatically at elevated temperatures.[1] The reaction can be written as



$$^{-}OOCCH_2\underset{^{+}NH_3}{CH}COO^{-} \rightleftarrows {}^{-}OOCCH{=}CHCOO^{-} + NH_4^{+} \quad (1)$$

The equilibrium constant for the reaction has been measured[2] between 5 and 135°. This reversible deamination of aspartic acid differs from the decomposition of the other amino acids found in proteins. Most other amino acids undergo a slow irreversible decarboxylation.[3] The kinetics for this nonenzymatic reversible deamination of aspartic acid and the equilibrium constant have been used to estimate the minimum ammonium ion concentration in the oceans of the primitive earth.[1] We report here further investigations of the kinetics and mechanics of this reaction.

The rate of deamination of aspartic acid was studied between pH −1 and 13 over the temperature range 60 to 135°. Solutions of DL-aspartic acid, buffered by either hydrochloric acid, succinate, phosphate, borate, or NaOH, were used for the determinations.[4] The final ionic strength was adjusted to 0.1 by adding sodium chloride. The solutions were deoxygenated and sealed under vacuum in glass ampoules. Values of k_{deam}, the first-order rate constant for deamination, were determined from measurements of the rate of appearance

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[1] J. L. Bada, and S. L. Miller, *Science*, **159**, 423 (1968).

[2] J. L. Bada and S. L. Miller, *Biochemistry*, **7**, 3403 (1968).

[3] P. H. Abelson in "Researches in Geochemistry," P. H. Abelson, Ed., John Wiley & Sons, Inc., New York, N. Y., 1959, p 79; J. R. Vallentyne, *Geochem. Cosmochim. Acta*, **28**, 157 (1964); D. Conway and W. F. Libby, *J. Amer. Chem. Soc.*, **80**, 1077 (1958).

[4] The pH values of the HCl, phosphate, borate, and carbonate buffers at the various temperatures were determined by extrapolation of data taken from R. G. Bates, G. D. Pinching, and E. R. Smith, *J. Res. Natl. Bur. Std.*, **45**, 418 (1950), and R. G. Bates, "Determination of pH," John Wiley & Sons, Inc., New York, N. Y., 1964, p 76; the pH values of the succinate buffers as a function of temperature were determined from measurements described previously[2] and from the data of R. G. Bates and R. Gary, *J. Res. Natl. Bur. Std.*, **65A**, 495 (1961); the pH of the NaOH buffers at the elevated temperatures were calculated from the temperature variation of pK_w given in R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Butterworth & Co. (Publishers), London, 1959, p 544.