A Study of Transient Phenomena in the Reactions of Alkoxy Radicals with Triphenylphosphine and Triphenylborane

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Abstract: Alkoxytriphenylphosphoranyl and boranyl radicals have been observed using optical absorption spectroscopy. Kinetic measurements of the formation of these species provide the first absolute measurements of radical attack at the phosphorus and boron centers. For *tert*-butoxy radical attack at 22 °C the rate constants are 1.9×10^9 and 1×10^8 $M^{-1}\,s^{-1}$ for Ph_3P and Ph_3B, respectively. The radicals so produced decay with lifetimes of 900 and 15 μs, respectively. Methoxytriphenylphosphoranyl radicals are produced in the radiolysis of methanolic solutions of triphenylphosphine; a reinterpretation of earlier experiments in the field is suggested. In the case of triphenylphosphine the radicals have been examined using laser flash photolysis, ESR spectroscopy, pulse radiolysis, and conventional flash photolysis, the various techniques providing mutually supporting results. In the case of triphenylborane our results provide for the first time conclusive evidence for the stepwise nature of radical reaction at the boron center.

Many free-radical reactions of organophosphorus compounds are known to involve the intermediacy of tetracoordinated phosphoranyl radicals of the type $X\dot{P}R_3$,[3-5] where X is frequently an alkoxy group. A number of studies have characterized phosphoranyl radicals using ESR techniques and have also examined the kinetics and mechanism of their decay processes.[4] However, phosphoranyl radicals have never been conclusively characterized using optical spectroscopy. Further, no absolute measurements of their rates of formation have been carried out, and the literature on aryl-substituted radicals is noticeably scarce.[5,6]

Phosphoranyl radicals typically decay by α- or β-cleavage (reactions 1 and 2).[3] The former frequently leads to overall processes which can be regarded as S_H2 reactions at the phosphorus center.

$$t\text{-BuO}\cdot + PR_3 \rightarrow t\text{-BuO}\dot{P}R_3 \rightarrow t\text{-BuOPR}_2 + R\cdot \tag{1}$$

$$t\text{-BuO}\cdot + PR_3 \rightarrow t\text{-BuO}\dot{P}R_3 \rightarrow OPR_3 + t\text{-Bu}\cdot \tag{2}$$

Substitution reactions of the type illustrated by reaction 1 are quite common throughout organometallic chemistry;[3b] for example, the substitution reactions of free radicals at the boron center in organoboranes are among the most thoroughly studied examples of bimolecular homolytic substitution.[7-9] In particular, the reaction of organoboranes with *tert*-butoxy radicals has received considerable attention.[7] The presence of a vacant p orbital at the boron center and the well-known stability of trialkylborane–amine complexes (e.g., Me_3B:pyridine)[10] have led to the speculation that the reaction involves a tetracoordinate intermediate, but such species have not, so far, been detected.[7,9] Reaction 3 illustrates the mechanism for the case of the *tert*-butoxy radical attack.

$$t\text{-BuO}\cdot + R_3B \rightarrow [t\text{-BuO}\dot{B}R_3] \rightarrow t\text{-BuOBR}_2 + R\cdot \tag{3}$$

In this paper we report a kinetic and spectroscopic study of the reactions of alkoxy radicals with triphenylphosphine and triphenylborane. With the phosphine we have used the techniques of laser and conventional flash photolysis, pulse radiolysis, and electron spin resonance to identify the phosphoranyl radical, $t\text{-BuO}\dot{P}Ph_3$ (**1**), as well as to study its formation and decay. Together these various techniques give a detailed understanding of the processes involved in the reaction of alkoxy radicals with triphenylphosphine providing as they do corroborative information concerning the mechanisms involved.

In the case of triphenylborane, we have examined its reaction with *tert*-butoxy radicals using nanosecond laser flash photolysis. From these experiments we have obtained conclusive evidence showing that the stepwise mechanism proposed (reaction 3) is correct. We have examined the formation and decay kinetics of the intermediate boranyl radical $t\text{-BuO}\dot{B}Ph_3$ (**2**), as well as its absorption spectra. The choice of triphenylborane as the substrate was based on our expectation that the strong bond between the phenyl group and the boron atom would make the transient relatively long lived, while the presence of the aromatic rings would facilitate detection by optical methods.

Results

This section has been divided according to the experimental technique used. All experiments have been carried out under oxygen-free conditions.

Laser Flash Photolysis. *tert*-Butoxy radicals were generated by photodecomposition of freshly purified di-*tert*-butyl peroxide using pulses (337.1 nm, 8 ns, ~3 mJ) from a nitrogen laser; associated transient absorptions were monitored using a detection system with nanosecond response (see Experimental Section for details).

Transient intermediates characterized by easily detectable absorptions were observed with both triphenylphosphine and triphenylborane. The growths of these transient absorptions follow clean first-order kinetics and are considerably faster than their decay. The rate constant associated with transient formation incorporates information on the rate constant, k_r, for attack at the metal center as well as on the rates of all other possible modes of first- (or pseudo-first-) order decay of the *tert*-butoxy radicals[11] represented by reaction 4, where τ is the *tert*-butoxy radical lifetime in the absence of substrate; in the solvent used (1:2 benzene-di-*tert*-butyl peroxide) it can be expected to be largely determined by hydrogen abstraction from di-*tert*-butyl peroxide, with minor contributions from β-cleavage, reaction 5.

$$t\text{-BuO}\cdot \xrightarrow{\tau^{-1}} \text{first-order decay} \tag{4}$$

$$t\text{-BuO}\cdot \rightarrow CH_3COCH_3 + CH_3\cdot \tag{5}$$

Assuming that the generation of *tert*-butoxy radicals is much faster than their decay, a simple first-order treatment of the kinetic data leads to the equation[11,13]

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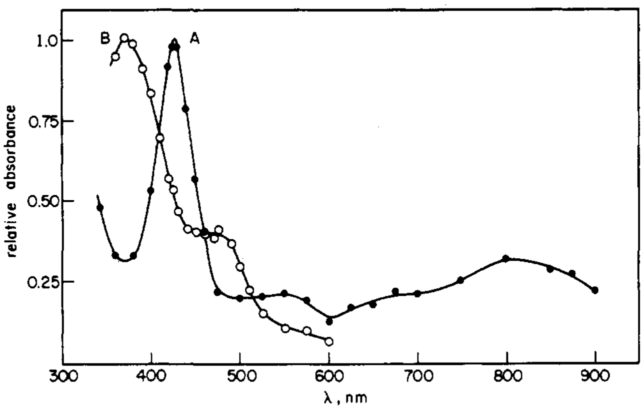

Figure 1. Transient absorptions due to $t\text{-BuO}\dot{\text{P}}\text{Ph}_3$ (A) and $t\text{-BuO}\dot{\text{B}}\text{Ph}_3$ (B) determined using laser flash photolysis.

$$k_{\text{expt}} = \tau^{-1} + k_r[\text{Ph}_3\text{M}] \qquad \text{(I)}$$

where M is phosphorus or boron and k_{expt} is the first-order rate constant determined using the equation

$$\ln \frac{A_\infty}{A_\infty - A} = k_{\text{expt}}t \qquad \text{(II)}$$

A_∞ and A are transient optical densities for $t\text{-BuO}\dot{\text{M}}\text{Ph}_3$ at its maximum, A_∞, on the "plateau" and at time t, respectively.

It should be remarked that for this treatment to be valid the *tert*-butoxy radicals must decay solely by first- or pseudo-first-order processes. A study of the time profiles' dependence on the energy of the incident laser pulse confirmed that this criterion is met in the systems under study.[11]

1. Triphenylphosphine. Laser excitation of solutions of triphenylphosphine in 1:2 benzene-*t*BuOOBu-*t* (v/v) leads to the transient spectrum shown in Figure 1A. The extinction coefficient at the maximum is ϵ_{430} ~6200 M^{-1} cm^{-1} and was obtained by comparison with diphenylhydroxymethyl radicals generated through reaction of *tert*-butoxy radicals with diphenylmethanol (see Experimental Section). The transient formed by reaction of *tert*-butoxy radicals with triphenylphosphine is assigned to **1**. We note that the spectrum of Figure 1A is different from that reported for the triphenylphosphine radical cation.[14]

Figure 2 includes a representative plot for the determination of k_{expt}, while Figure 3 illustrates the evaluation of k_r (M = P) and τ. The value for $[\text{Ph}_3\text{M}] = 0$ was measured in a previous study with diphenylmethanol.[11] From the kinetic analysis outlined above a rate constant of 1.9×10^9 M^{-1} s^{-1} was obtained for *tert*-butoxy radical attack on Ph_3P at room temperature.

2. Triphenylborane. The purification and handling of triphenylborane proved to be critical in achieving reproducibility in the kinetic measurements. The commercial product has usually been exposed to air, which results in extensive superficial oxidation. The solid can be handled briefly under dry air, but solutions must be prepared under oxygen-free conditions.

Laser excitation of triphenylborane in solution produces a transient with significant absorption at λ <530 nm. The spectrum of this species, which we believe to be $t\text{-BuO}\dot{\text{B}}\text{Ph}_3$, is shown in Figure 1B.

The absorption spectrum of this transient is independent of the concentration of Ph_3B (range examined: $0.12 < [\text{Ph}_3\text{B}] < 0.97$ M). Its intensity increases with increasing Ph_3B concentration.

The rate constant for attack of *tert*-butoxy radicals at the boron center was measured as $k_r = 1.0 \times 10^8$ M^{-1} s^{-1}. Representative kinetic plots using I and II are shown in Figures 2 and 3.

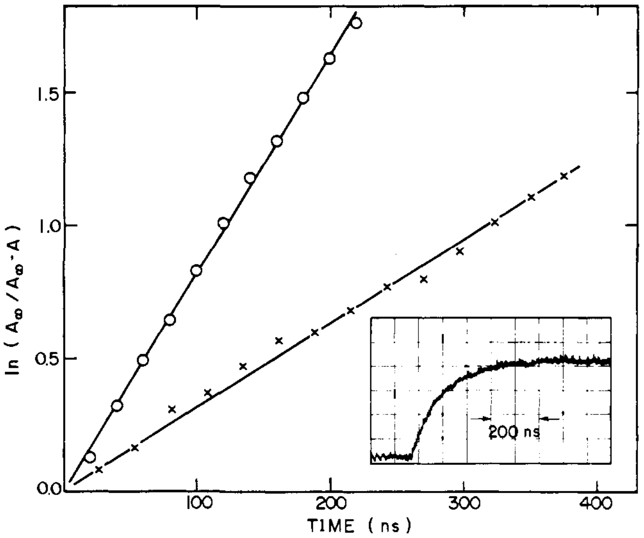

Figure 2. Determination of k_{expt} for Ph_3P, 0.0044 M (X), and Ph_3B, 0.027 M (O), according to eq II. Insert: representative oscilloscope trace for Ph_3P.

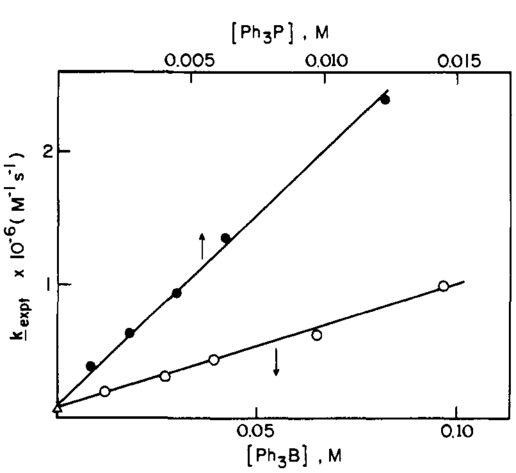

Figure 3. Determination of k_r for Ph_3P (●) and Ph_3B (○) according to eq I. The intercept (△) was taken from ref 11.

Triphenylborane has been shown to react with *tert*-butoxy radicals in the same manner as other organoboranes;[7b] therefore, the decay of $t\text{-BuO}\dot{\text{B}}\text{Ph}_3$ must occur according to the reaction

$$t\text{-BuOBPh}_3\ (\mathbf{2}) \xrightarrow{k_d} t\text{-BuOBPh}_2 + \text{Ph}\cdot \qquad (6)$$

While individual decay plots show reasonably clean first-order kinetics, changes in the initial concentration of $t\text{-BuO}\dot{\text{B}}\text{Ph}_3$ produced by suitable adjustment of the laser intensity indicate a slight dependence on concentration and lead to an order of 1.15 for decay. The half-life ($t_{1/2}$) extrapolated to zero radical concentration is 10.5 μs, which gives $k_d = 6.6 \times 10^4$ s^{-1}. The purification of triphenylborane was seemingly more critical for the evaluation of k_d than for k_r.

Conventional Flash Photolysis. All experiments described in this section refer to triphenylphosphine. The samples were excited by flashes from two xenon lamps parallel to the sample cell (60–250 J, ~40 μs, naphthalene in methanol was used as a cutoff filter). We have found (vide infra) that the relatively long lifetime of the phosphoranyl radical makes it more suitable for this technique than for laser photolysis because the longer optical path (200 vs. 3 mm) allows the use of lower radical concentrations, thus preventing kinetic interference

Table I. Rate Constants for Decay of Phosphoranyl and Boranyl Radicals

radical	temp/K	k, s^{-1}	solvent and methods
1	295	1110	benzene-t-BuOOBu-t, flash photolysis
4	295	750	methanol, pulse radiolysis
1	272	87.7	toluene, ESR
1	263	39.6	toluene, ESR
1	253	12.9	toluene, ESR
1	241	5.59	toluene, ESR
1	239	4.18	toluene, ESR
1	232	2.17	toluene, ESR
1	225	1.28	toluene, ESR
2	295	66 000	benzene-t-BuOOBu-t, laser photolysis

from second-order processes. Under these conditions we observed simple first-order decays of $t\mathrm{BuO\dot{P}Ph_3}$ over more than 5 half-lives and initial radical concentrations which varied by a factor of ca. 4. Kinetic analysis leads to $k_d = 1110\ \mathrm{s^{-1}}$ at room temperature.

$$t\text{-BuO}\dot{\mathrm{P}}\mathrm{Ph_3} \xrightarrow{k_d} t\text{-Bu}\cdot + \mathrm{OPPh_3} \qquad (7)$$

The "end-of-pulse" spectrum observed in these experiments agrees well with the "plateau" spectrum obtained in the laser experiments and shown in Figure 1.

When the decay of **1** is monitored in the 400-nm region we observe a residual absorbance which corresponds to the yellowish coloration of the irradiated solutions. This coloration is bleached in a few minutes when the samples are exposed to air.

Electron Spin Resonance. UV irradiation of toluene solutions of di-*tert*-butyl peroxide and triphenylphosphine in the cavity of an ESR spectrometer gave the spectrum characteristic of **1** ($a^{\mathrm{P}} = 45.0$ G at -80 °C).[5] The decay kinetics of **1** were monitored using the standard rotating sector technique.[15] In the temperature range -60 to -80 °C, the decay of **1** exhibited a significant contribution from a second-order process at relatively high radical concentrations ($\sim 10^{-5}$ M). This is presumably due to the loss of **1** via bimolecular self-reaction. By contrast, **1** decays with clean first-order kinetics over at least 3 half-lives in the range -40 to 0 °C. In addition, the concentration of **1** was proportional to the incident light intensity and the first-order rate constants for its decay were independent of reactant concentrations. Table I gives a summary of the rates of decay for **1**. These results are entirely consistent with the rate constant observed at 22 °C using flash photolysis techniques.

Attempts to characterize **2** using ESR spectroscopy have so far been fruitless.[16]

Pulse Radiolysis. In a recent study of the radiolysis of methanolic solutions of triphenylphosphine, Brescia et al.[17] observed a transient intermediate which they suggested to be $\mathrm{Ph_3\dot{P}CH_2OH}$ (**3**). The close similarity between the spectrum of Figure 1A and that reported for **3** led us to believe that the species observed was in fact $\mathrm{CH_3O\dot{P}Ph_3}$ (**4**), and not **3**. We therefore undertook some pulse radiolysis experiments on $\mathrm{Ph_3P}$ in $\mathrm{N_2O}$-saturated methanol. The same transient absorptions were observed as those reported by Brescia et al.[17] However, under our conditions the decay of the transient was predominantly first order [with minor (<30%) contributions from second order] whereas Brescia et al. have observed principally second-order processes. This difference is not surprising since their radiation doses were considerably higher than ours (10 000 vs. 600 rad). The rate of decay measured at the lowest "workable" radical concentration gave $k_d \simeq 750\ \mathrm{s^{-1}}$ in methanol at room temperature. In order to establish further the mechanism of reaction we carried out experiments in both methanol and in methanol d_4 using a Stern-Volmer approach for treatment of the data. If the reaction intermediate was **3**, little or no isotope effect would be anticipated on the Stern-Volmer slope, since the lifetime of its precursor would not involve hydrogen transfer. If the species is **4** (see reaction 8) we would expect an isotope effect reflecting the decay of $\mathrm{CH_3O}$ via reaction 9. The yields of $\mathrm{CH_3O}$ and $\mathrm{\dot{C}H_2OH}$ in methanol have been reported as 2.0 and 7.4, respectively.[18]

$$\mathrm{CH_3O\cdot + PPh_3 \xrightarrow{k_r} CH_3O\dot{P}Ph_3}\ (\mathbf{4}) \qquad (8)$$

$$\mathrm{CH_3O\cdot + CH_3OH \xrightarrow{k_a} CH_3OH + \dot{C}H_2OH} \qquad (9)$$

$$G = G^0 \frac{k_r[\mathrm{PPh_3}]}{k_a[\mathrm{CH_3OH}] + k_r[\mathrm{Ph_3P}]} \qquad \text{(III)}$$

G is the yield of **4**, G^0 is the yield of methoxy radicals, and the product $k_a[\mathrm{CH_3OH}]$ is the reciprocal of the lifetime of methoxy radicals in methanol, which has been reported to be 106 ns.[18] A similar equation would hold for the deuteriosolvent, except that the lifetime of methoxy-d_3 radicals should be substantially longer as a result of the isotope effect on k_a. Figure 4 shows a plot according to the equation

$$\frac{\alpha}{G} = \frac{\alpha}{G_0} + \frac{\alpha}{G_0}\frac{1}{\tau k_r[\mathrm{Ph_3P}]} \qquad \text{(IV)}$$

where α is a constant and

$$\tau^{-1} = k_a[\mathrm{CH_3OH}] \text{ or } k_a'[\mathrm{CD_3OD}] \qquad \text{(V)}$$

The plot for methanol gives $k_r\tau = 540\ \mathrm{M^{-1}}$, which combined with $\tau = 106$ ns gives $k_r = 5.1 \times 10^9\ \mathrm{M^{-1}\ s^{-1}}$, a value in reasonable agreement with that measured for *tert*-butoxy radicals (vide infra). The intercept-to-slope ratio for methanol-d_4 gives $k_r\tau_d = 1080\ \mathrm{M^{-1}}$. Assuming that the change in the Stern-Volmer slope reflects only changes in τ, we obtain an isotope effect for reaction 9 of 2.0 ± 0.3.

Finally, experiments in $\mathrm{N_2O}$-saturated water-methanol mixtures containing $\mathrm{Ph_3P}$ in the 10 μM-1 mM range showed no evidence for the transient observed in pure methanol solutions. In such mixtures the predominant radical species should be $\mathrm{\dot{C}H_2OH}$ via reactions 10 and 11.

$$\mathrm{e^-_{aq} + N_2O + H_2O \rightarrow \cdot OH + OH^- + N_2} \qquad (10)$$

$$\mathrm{\cdot OH + CH_3OH \rightarrow \dot{C}H_2OH + H_2O} \qquad (11)$$

Discussion

Generation of the Radicals. A number of earlier studies have been concerned with rates of alkoxy radical attack at phosphorus and boron centers.[3,7,9] They have generally been based on competitive techniques, e.g., attack at the metal center vs. hydrogen abstraction from cyclopentane.[7] Our recent measurements of the absolute rates of reaction of *tert*-butoxy radicals with hydrocarbons (including cyclopentane) allow us to put those earlier values on an absolute scale.[11] Table II shows a summary of these rate parameters. Alkoxy radical attack at both centers is extremely fast, and the reaction with organophosphorus compounds approaches the diffusion-controlled limit.

We have also included in Table II rate constants involving the transient observed in the radiolysis of methanolic solutions of triphenylphosphine. We assign these to **4**, rather than **3**, on the following basis: (a) The radicals are not formed in aqueous methanol ($\mathrm{N_2O}$ saturated), where the attack of $\mathrm{\dot{O}H}$ on methanol produces hydroxymethyl radicals quite efficiently. (b) The precursor has a longer lifetime in methanol-d_4 than in methanol, a characteristic which should be associated to methoxy rather than hydroxymethyl radicals. (c) We do not

Table II. Representative Rate Constants for Alkoxy Radical Attack at the Phosphorus and Boron Centers at Room Temperature

radical	X_3M	k, $M^{-1}\,s^{-1}$	source
t-BuO·	Ph_3P	1.9×10^9	laser photolysis
MeO·	Ph_3P	5.1×10^9	pulse radiolysis
t-BuO·	$P(OEt)_3$	8.1×10^8	ESR competition with cyclopentane[a,b]
t-BuO·	PEt_3	1.2×10^9	ESR competition with $P(OEt)_3$[c]
t-BuO·	Ph_3B	1.0×10^8	laser photolysis
t-BuO·	n-Bu_3B	1.5×10^8	ESR competition with cyclopentane[a,d]
t-BuO·	i-Bu_3B	5.1×10^6	ESR competition with cyclopentane[a,d]
t-BuO·	sec-Bu_3B	1.5×10^6	ESR competition with cyclopentane[a,d]
t-BuO·	$(MeBO)_3$	1.0×10^7	ESR competition with cyclopentane[a,d]

[a] Competitive rate measurements from the original publication combined with the rate for cyclopentane from laser photolysis measurements.[11] The analysis usually assumes that the intermediate decays solely to give scission products, a condition which is met at low radical concentrations. [b] References 4b and 4d. [c] Reference 4f. [d] Reference 8e.

observe significant changes in the radical yields when the radiation dose is changed, which would indicate that the precursor decays in pseudo-first-order processes. (d) The rate of reaction (5.1×10^9 M^{-1} s^{-1}) seems consistent with rates observed in analogous *tert*-butoxy radical reactions. (e) The spectrum observed is very similar to that of Figure 1A. (f) The suggestion of an alkoxyphosphoranyl intermediate is consistent with the observation that methane is among the products of reaction ($G_{CH_4} = 0.8$),[18] since methyl radicals can be expected to result by β-scission of **4**.

Our results provide definite evidence for the involvement of a discrete intermediate in the reaction of *tert*-butoxy radicals on triphenylborane. The kinetics observed (Table II) agree well with relative reactivities reported earlier.[7b] Unfortunately, we were unable to obtain ESR evidence to confirm our assignment of this transient to $Bu^tO\dot{B}Ph_3$, though it should be noted that the short lifetime observed is expected to make ESR detection difficult. We believe that the combination of kinetic and spectroscopic results presented here, as well as the mechanism of reaction, which has been established by Davies et al.,[7b] leads to the rather unequivocal characterization of the boranyl radical. Two alternative explanations are worth considering and we believe both can be disregarded: (1) It could be suggested that the transient arises from a reaction of $Bu^tO\cdot$ different from the one proposed. This seems highly unlikely since the mechanism of reaction is known in addition to the fact that *tert*-butoxy radicals are not prone to ring addition, the only other process that could be proposed. Further, the spectrum in Figure 1 does not resemble a cyclohexadienyl-type radical and is too intense for a radical of this nature. (2) The other possible suggestion would be that, even if *tert*-butoxy does react in the expected manner to yield phenyl, the species observed is actually the result of further attack of phenyl radicals on Ph_3B. Again, this is virtually impossible: our data (Figure 3) extrapolate to the same intercept measured in the reaction of $Bu^tO\cdot$ with Ph_3P and diphenylmethanol,[11] this number being characteristic of *tert*-butoxy, not phenyl; in addition, our kinetic studies indicate that the *precursor* of the radical detected must be produced "instantaneously" in the time scale of our experiments, which is again consistent with *tert*-butoxy, not phenyl. Finally, phenyl radicals are likely to add to the abundant benzene (3.5 M) or abstract hydrogen from the peroxide (3.6 M).

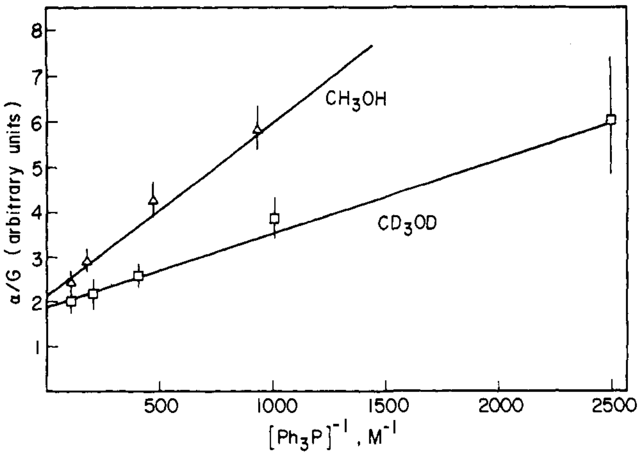

Figure 4. Effect of Ph_3P concentration on the yields of **4**, according to eq IV.

All the evidence given above leads us to conclude that the transient observed following laser excitation of the peroxide-Ph_3B system is indeed the boranyl radical. Previous studies, largely by Davies and co-workers, showed that the substitution at boron is a sterically controlled process,[7,8] while the energy of the bond cleaved in the scission step seems to be unimportant. This is in fact to be expected if bond breaking is not the rate-determining step; the lifetime of **2**, rather than its formation, should depend on the B-C bond energy.

The only other reaction at the boron center where we obtained indirect evidence for a stepwise process is the reaction of trialkylboranes with the triplet state of aromatic ketones. In such systems the reaction occurs with high rate constants but low quantum efficiencies.[19]

Spectroscopic Properties. The ESR spectra of **1** show an unusually low a_p coupling constant.[5] This has been attributed to a radical structure in which the unpaired electron is centered largely on the aromatic rings, and it has been speculated that these radicals would have tetrahedral rather than the typical trigonal bipyramidal structure. The strong optical absorptions that extend well into the near-infrared region presumably reflect the same effect, i.e., electron delocalization into the aromatic π orbitals. It seems possible that this property could be exhibited by a wide range of aromatic phosphoranyl radicals, which would make their spectroscopic detection straightforward.

To the best of our knowledge the spectrum shown in Figure 1B is the only one of its kind reported; as a result there is no possibility for comparison with related radicals.

Decay Kinetics. Walling and Pearson[20] have established that **1** decays via β-scission, an observation that is also consistent with the conclusion by Davies et al.[21] that phenyl substituted phosphoranyls undergo β-scission efficiently. The rates of decay of **1** are given on Table I. On the critical assumption that the mechanism of reaction does not change when the temperature is lowered, from an Arrhenius plot (Figure 5 and Table I) we obtain

$$k_d\,(s^{-1}) = 10^{11.7} \exp(-12\,100/RT) \text{ for } \mathbf{1}$$

Figure 5 illustrates the excellent agreement obtained between the techniques used, which makes us confident of our spectral assignments, a conclusion which can probably be extended to the boranyl radical as well.

Our results, both from ESR and pulse radiolysis experiments, indicate that a second-order decay process can also be of importance at low temperatures or high excitation doses. Pulse radiolysis experiments indicate that, if **4** has an extinction coefficient of the same order of magnitude as **1**, the second-order decay must have a rate constant in the neighborhood of

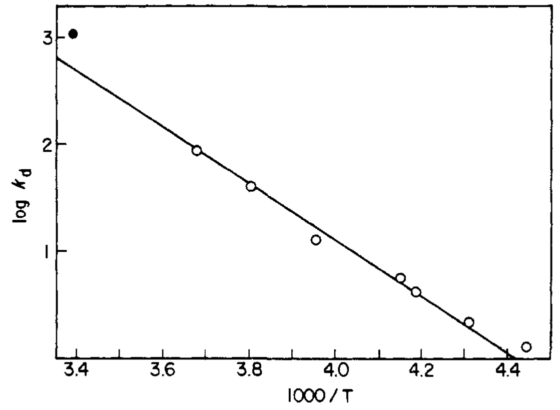

Figure 5. Arrhenius plot for the decay of **1**: (○), ESR data; (●), laser photolysis.

10^9 M^{-1} s^{-1} in order for the decay of **4** to have some contribution from second-order processes under our experimental conditions. Similar rates have been reported for other organophosphorus radicals.[4c,g]

It should be noted that the radicals produced in the decay of **1** and **2** can in principle undergo cross-termination reactions with **1** or **2**. This is unlikely in the case of **2** because of its short lifetime, but in the case of **1** reaction 12 seems quite probable.

$$t\text{-Bu}\cdot + t\text{-BuO}\dot{\text{P}}\text{Ph}_3 \rightarrow \text{products} \qquad (12)$$

Under these conditions the apparent kinetics would still be first order, but the actual k_d would be smaller than the measured value (one-half in the limiting case). This type of error would be expected to affect the preexponential factor but not the activation energy.

The radical t-BuO$\dot{\text{B}}$Ph$_3$, while considerably shorter lived than the analogous phosphoranyl radical, is still long lived enough that one could hope to detect it using ESR techniques. Experiments of this type have so far been unsuccessful, reflecting probably the complexity which results from side reactions of the displaced phenyl radicals when the process is not examined immediately following the generation of the alkoxy radicals. If the preexponential factor for the decomposition of **2** can be taken as ca. 10^{12} M^{-1} s^{-1}, then the activation energy for reaction 6 would be in the neighborhood of 10 kcal/mol. Other radicals of this type can be expected to be shorter lived (e.g., t-BuO$\dot{\text{B}}$Et$_3$) as a result of their lower B–C bond energy.

Conclusion

Alkoxytriphenylphosphoranyl radicals show strong absorption bands in the visible region of the spectrum ($\lambda_{\max}$ 430 nm, $\epsilon_{\max}$ ~6200 M^{-1} cm^{-1} for **1**) which extend well into the near-IR region; these characteristics probably reflect an extensive delocalization of the unpaired electron on the aromatic rings and are consistent with the low values of the ^{31}P hyperfine coupling constants.[5]

Our results for triphenylborane provide conclusive evidence for the stepwise nature of the reaction with *tert*-butoxy radicals. In fact, the behavior of triphenylborane parallels that of phosphorus compounds, though it is clear that the tetracoordinate boranyl radical intermediate is considerably less stable than its phosphorus counterpart.

The rates of reaction of alkoxy radicals with triphenylphosphine are almost diffusion controlled and are among the fastest known radical-molecule reactions. High rates are also observed with other organophosphorus compounds as well as organoboranes.

Experimental Section

Materials. Triphenylphosphine (Aldrich) was recrystallized from ethanol or sublimed. Di-*tert*-butyl peroxide (MCB) was treated on an alumina column and distilled. Methanol and benzene were Aldrich Gold Label and were used as received. Methanol-d_4 was an Aldrich product with 99+% isotopic purity. Triphenylborane (Aldrich) was sublimed twice under high vacuum conditions. A sample which was zone refined (30 cycles) and then sublimed twice gave consistent results.

Laser Photolysis. A Molectron UV-400 nitrogen laser was used for excitation (337.1 nm, ~8 ns, ~3 mJ). In the case of triphenylphosphine the samples were contained in a 3 × 7 mm cell, made of Suprasil quartz, which was part of a flow system. Helium gas was bubbled through the solutions in a container directly attached to the reaction cell. The pulses from the nitrogen laser were incident on the sample at ~15°. The monitoring beam consisted of a pulsed Eimac 150-W xenon lamp, a Bausch & Lomb high-intensity monochromator, and an RCA-4840 photomultiplier tube. The signal from the detector was terminated with 93 Ω and into a Tektronix 7623 storage oscilloscope. Averaging techniques were similar to those described previously.[11]

In the case of triphenylborane a specially designed cell was used for the experiments. The solid triphenylborane was weighed into a Suprasil quartz cell which was then connected with an Ace Glass Teflon adaptor to the main sample tube which in turn contained the benzene-di-*tert*-butyl peroxide mixture. The solvent was then degassed by three freeze-pump-thaw cycles to a residual pressure of less than 10^{-5} Torr. The solution was then prepared under high vacuum conditions. Total exposure time of the solid triphenylborane to air was usually in the neighborhood of 1 min.

ESR Experiments. In a typical experiment, a solution of triphenylphosphine (~0.1 M) in di-*tert*-butyl peroxide and toluene (1:3 v/v) was passed via a flow system (flow rate 0.2 mL/min) through the cavity of a Varian E104 spectrometer. Direct UV photolysis in the ESR cavity gave an intense spectrum of **1**. The decay kinetics were measured using the standard rotating sector procedure.[15]

Pulse Radiolysis. These measurements were carried out using a computerized system similar to that described earlier.[22] The apparatus now makes use of the Notre Dame 10-MeV linear accelerator with the capability of providing 5-ns pulses. A flow system was used to assure that fresh solution was brought to the radiolysis cell between electron pulses. All the experiments described have been carried out in N$_2$O-saturated solutions.

Most experiments were carried out in a 2-cm long cell, with the exception of those using methanol-d_4 and the matched experiments using methanol, where the optical path was reduced to 0.5 cm to minimize the cost of the solvent. Typically 20–60 pulses were averaged for each measurement.

Conventional Flash Photolysis. The system used had an optical pathway of 200 mm and a time resolution of ca. 40 μs. A more detailed description can be found elsewhere.[23]

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References and Notes

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(2) (a) The research described herein was supported by the Office of Basic Energy Sciences of the Department of Energy. This is Document No. NDLR-1938 from the Notre Dame Radiation Laboratory. (b) Issued as NRCC Publication No. 17487.

(3) (a) W. G. Bentrude in "Free Radicals", Vol. II, J. K. Kochi, Ed., Wiley, New York, 1973, Chapter 22; (b) K. U. Ingold and B. P. Roberts, "Free Radical Substitution Reactions", Wiley-Interscience, New York, 1971.

(4) (a) J. K. Kochi and P. J. Krusic, *J. Am. Chem. Soc.*, **91**, 3944 (1969); (b) A. G. Davies, D. Griller, and B. P. Roberts, *Angew. Chem., Int. Ed. Engl.*, **10**, 738 (1971); (c) G. B. Watts, D. Griller, and K. U. Ingold, *J. Am. Chem. Soc.*, **94**, 8784 (1972); (d) A. G. Davies, D. Griller, and B. P. Roberts, *J. Chem. Soc., Perkin Trans. 2*, 993 (1972); (e) D. Griller and B. P. Roberts, *J. Organomet. Chem.*, **42**, C47 (1972); (f) A. G. Davies, R. W. Dennis, D. Griller, and B. P. Roberts, *ibid.*, **40**, C33 (1972); (g) D. Griller and B. P. Roberts, *J. Chem. Soc., Perkin Trans. 2*, 1416 (1972); (h) *ibid.*, 1339 (1973); (i) A. G. Davies, R. W. Dennis, and B. P. Roberts, *ibid.*, 1101 (1974); (j) D. Griller, B. P. Roberts, A. G. Davies, and K. U. Ingold, *J. Am. Chem. Soc.*, **96**, 554 (1974); (k) D. Griller and K. U. Ingold, *ibid.*, **97**, 1813 (1975); (l) J. W. Cooper and B. P. Roberts, *J. Chem. Soc., Perkin Trans. 2*, 808 (1976); (m) J. W. Cooper, M. J. Parrott, and B. P. Roberts, *ibid.*, 730 (1977).

(5) A. G. Davies, M. J. Parrott, and B. P. Roberts, *J. Chem. Soc., Chem. Commun.*, 973 (1974).

(6) A. G. Davies, M. J. Parrott, and B. P. Roberts, *J. Chem. Soc., Perkin Trans. 2*, 1066 (1976).

(7) (a) A. G. Davies and B. P. Roberts, *Acc. Chem. Res.*, **5**, 387 (1972); (b) A.

G. Davies and B. P. Roberts in "Free Radicals", Vol. I, J. K. Kochi, Ed., Wiley, New York, 1973, Chapter 10.

(8) (a) K. U. Ingold. *Chem. Commun.*, 911 (1969); (b) A. G. Davies, K. U. Ingold, B. P. Roberts, and R. Tudor, *J. Chem. Soc. B*, 698 (1971); (c) S. Korcek, G. B. Watts, and K. U. Ingold, *J. Chem. Soc., Perkin Trans. 2*, 242 (1972); (d) J. Grotewold, E. A. Lissi, and J. C. Scaiano, *J. Chem. Soc. B*, 475 (1969); (e) A. G. Davies, D. Griller, and B. P. Roberts, *ibid.*, 1823 (1971); (f) A. G. Davies, T. Maki, and B. P. Roberts, *J. Chem. Soc., Perkin Trans. 2*, 744 (1972); (g) A. G. Davies, D. Griller, B. P. Roberts, and R. Tudor, *Chem. Commun.*, 640 (1970); (h) J. Grotewold, E. A. Lissi, and J. C. Scaiano, *J. Chem. Soc. B*, 1187 (1971); (i) A. G. Davies and J. C. Scaiano, *J. Chem. Soc., Perkin Trans. 2*, 2234 (1972).

(9) P. J. Krusic and J. K. Kochi, *J. Am. Chem. Soc.*, **91**, 3942 (1969); J. K. Kochi and P. J. Krusic, "Essays on Free-Radical Chemistry", *Chem. Soc. Spec. Publ.* **No. 24** (1970).

(10) H. C. Brown, "Hydroboration", W. A. Benjamin, New York, 1962; T. B. Eames and B. M. Hoffman, *J. Am. Chem. Soc.*, **93**, 3141 (1971).

(11) H. Paul, R. D. Small, Jr., and J. C. Scaiano, *J. Am. Chem. Soc.*, **100**, 4520 (1978).

(12) C. Walling and P. J. Wagner, *J. Am. Chem. Soc.*, **85**, 2333 (1963); **86**, 3368 (1964).

(13) R. D. Small, Jr., and J. C. Scaiano, *J. Phys. Chem.*, **81**, 828, 2126 (1977).

(14) T. Shida and W. H. Hamill, *J. Chem. Phys.*, **44**, 2369 (1966).

(15) K. Adamic, D. F. Bowman, T. Gillan, and K. U. Ingold, *J. Am. Chem. Soc.*, **93**, 902 (1971).

(16) The difficulty appears to arise in part from the low solubility of Ph_3B in di-*tert*-butyl peroxide.

(17) M. Venturi, A. Brescia, F. Busi, and Q. G. Mulazzani, *Int. J. Radiat. Phys. Chem.*, **8**, 673 (1976).

(18) D. H. Ellison, G. A. Salmon, and F. Wilkinson, *Proc. R. Soc. London, Ser. A*, **328**, 23 (1972), and references cited therein.

(19) A. G. Davies and J. C. Scaiano, *J. Chem. Soc., Perkin Trans. 2*, 2234 (1972).

(20) C. Walling and M. S. Pearson, *J. Am. Chem. Soc.*, **86**, 2262 (1964).

(21) Recent results indicate that the difference in the rates of β-scission between $PhP(OEt)_2OBu$-*t* and *t*-$BuOP(OEt)_3$ may be small (see also ref 5). We are grateful to Dr. B. P. Roberts for the communication of unpublished work.

(22) L. K. Patterson and J. Lilie, *Int. J. Radiat. Phys. Chem.*, **6**, 129 (1974); R. H. Schuler and G. K. Buzzard, *ibid.*, **8**, 563 (1976).

(23) G. Ferraudi, *Inorg. Chem.*, **17**, 1370 (1978).

Theoretical Investigations on Some C_2SiH_4 Isomers

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Abstract: A part of the C_2SiH_4 potential energy surface has been explored using a nonempirical pseudopotential method. The computed relative stabilities of the five isomers, silylacetylene (0 kcal/mol) < silacyclopropene (**3**) and silacyclopropylidene (**2**) (both 17 kcal/mol) < 2-silaallene (46 kcal/mol) < 2-silapropyne (61 kcal/mol), differ significantly from those of the analogous carbon compounds: propyne < allene < cyclopropene ≪ cyclopropylidene. Silacyclopropylidene (**2**) has a singlet while the carbene analogue a triplet ground state. The relative stabilities of the two cyclic structures **2** and **3** have been analyzed further using extensive CI calculations. The results do not suggest an aromatic character for **3**.

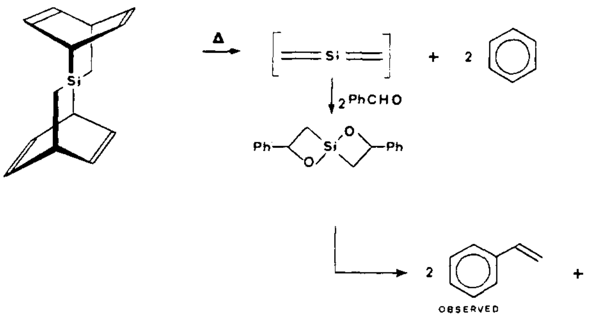
Introduction

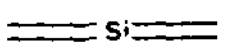
Silylacetylene (**5**) has been a well-known compound[2] for many years and its structure has been elucidated. More recently, derivatives of silacyclopropene (**3**) have been observed,[3] and in 1978 Bertrand, Manuel, and Mazerolles[4] suggested the existence of a digonal (i.e., sp-hybridized) silicon compound, 2-silaallene (**1**), as a possible intermediate in the copyrolysis of the adduct (2,8-dimethyl-3,9-dichloro-6-sila[5.5]spiroundecatetra-2,4,8,10-ene + methyl acetylenedicarboxylate) and benzaldehyde; see Scheme I.

In this context, we thought it might be of some interest to examine theoretically the existence and relative stability of such an intermediate in comparison with other possible isomers (especially those containing the C-Si-C linkage).

To this end, ab initio valence-only calculations have been carried out for the following C_2SiH_4 isomers: 2-silaallene (**1**), silacyclopropylidene (**2**), which is topologically very similar to the former, silacyclopropene (**3**), and 2-silapropyne (**4**), which also contain the C-Si-C linkage; as a test of reliability for the computational method used, silylacetylene (**5**), for which many experimental data are available, was also investigated.

Scheme I





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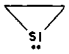

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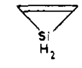

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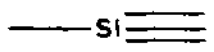

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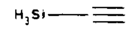

5

Method

All the SCF calculations were performed according to the PSIBMOL algorithm[5] using the pseudopotential method proposed by Durand and Barthelat.[6] This method is well adapted for calculations on molecules involving silicon atoms since it does not require more computing effort than for the analogous carbon compounds. Recent works[7] have shown that pseudopotential methods lead to results of the same quality as those obtained from an all-electron SCF method.

For each atom, the core electrons are taken into account through a nonempirical atomic pseudopotential determined from the double ζ atomic Hartree-Fock calculations of Clementi and Roetti.[8] The atomic pseudopotentials have the following analytical form:

$$W(r) = \sum_l W_l(r)P_l - z/r \qquad (1)$$

where z is the number of valence electrons for the neutral atom, P_l the projector on the lth subspace of the spherical harmonics, and