Absolute Rate Constants for the Autoxidation of Organometallic Compounds. Part II.[1] Benzylboranes and 1-Phenylethylboranes

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The kinetics for the free-radical chain autoxidation of several benzylboranes and 1-phenylethylboranes at 30° have been examined. The autoxidations of the dialkoxyboranes are highly autocatalytic. This is due both to an increasing rate of chain initiation and to an increasing oxidizability of the partially oxidized material as the reaction progresses. In the initial stages, chain propagation involves the abstraction of hydrogen from the carbon adjacent to the boron atom. It is postulated that as the oxidation proceeds hydrolysis and condensation reactions produce oxybisboranes and that these compounds are autoxidized *via* rapid S_H2 reactions at boron in which an alkylperoxyl radical replaces an alkyl radical. The final products are those that would be expected of an S_H2 reaction at boron in the starting compounds (alkylperoxydialkoxyboranes and mixed trialkoxyboranes).

The rate-controlling step for chain propagation in the autoxidations of the boroxines and of tribenzylborane involves peroxyl radical attack at boron. The following propagation rate constants were obtained: tribenzylboroxine, 1×10^6 l mol^{-1} s^{-1}; tri-(1-phenylethyl)boroxine, 4×10^6 l mol^{-1} s^{-1}; and tribenzylborane, 5×10^6 l mol^{-1} s^{-1}.

THE autoxidation of organoboron compounds in solution is a free-radical chain process.[1-5] At 30° and at oxygen partial pressures $\geqslant 150$ Torr the autoxidation of a variety of n-, s-, and t-butylboranes can be represented by the following reaction scheme.[1]

Initiation: Production of R· (Rate = R_i)

Propagation: $\text{R}\cdot + \text{O}_2 \longrightarrow \text{ROO}\cdot$

$\text{ROO}\cdot + \text{RB}\!< \xrightarrow{k_p} \text{ROOB}\!< + \text{R}\cdot$

Termination: $2\text{ROO}\cdot \xrightarrow{2k_t}$ Molecular products.

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[1] A. G. Davies, K. U. Ingold, B. P. Roberts, and R. Tudor, *J. Chem. Soc.* (*B*), 1971, 698 is considered to be Part I of this series.

[2] A. G. Davies and B. P. Roberts, *J. Chem. Soc.* (*B*), 1967, 17.

[3] A. G. Davies and B. P. Roberts, *J. Chem. Soc.* (*B*), 1969, 311.

[4] P. G. Allies and P. B. Brindley, *Chem. and Ind.*, 1967, 319; 1968, 1439; *J. Chem. Soc.* (*B*), 1969, 1126.

[5] K. U. Ingold, *Chem. Comm.*, 1969, 911.

The overall rate of oxidation, P, is given by

$$\frac{-\mathrm{d}[O_2]}{\mathrm{d}t} = P = \frac{k_p[\mathrm{RB}{<}]R_i^{\frac{1}{2}}}{(2k_t)^{\frac{1}{2}}}$$

In our previous kinetic work,[1] rates of oxidation of the butylboranes were measured at known rates of chain initiation. This allowed the ' oxidizability ', $k_p/(2k_t)^{\frac{1}{2}}$, of the different boranes to be calculated. Since values of $2k_t$ for the bimolecular self-reactions of primary, secondary, and tertiary butylperoxyl radicals were already known the propagation rate constants, k_p, for the bimolecular homolytic substitution (S_H2) by butylperoxyl radicals at the boron centre could be calculated. The magnitudes of these rate constants were found to be reduced by oxygen ligands on the boron and, for structurally analogous boranes, were influenced by counterbalancing electronic and steric effects in the butyl groups. The present work describes a study of the autoxidations of organoboranes having resonance-stabilized alkyl groups (benzyl and 1-phenylethyl) attached to boron.

EXPERIMENTAL

Materials.—The organoboranes studied in this work are listed in Table 1. They were all prepared, analysed, and handled under dry, oxygen-free, nitrogen, or argon. All solvents and materials used in the preparations of the organoboranes or of their solutions for the oxidation studies were dried and deoxygenated.

Tribenzylborane (1) was a gift from Dr. P. G. Allies. Benzylperoxydibenzylbrorane (2) was prepared in solution by the partial oxidation of (1) directly in the n.m.r. spectrometer.

The organoboranes (3)—(10) were prepared from the corresponding aralkyldihydroxyboranes, which were themselves stored in the form of their stable diethanolamine esters (11) and (12). The preparation of compound (12) has been described previously.[2] Compound (11) was prepared in an analogous manner.

The boroxines (3) and (4) were prepared by azeotropic dehydration of benzene solutions of the dihydroxyboranes. The n-butoxy-esters (7) and (10) were prepared by azeotropic dehydration of mixtures of n-butanol and the appropriate boroxine. Azeotropic dehydration of benzene solutions of dihydroxyboranes in the presence of ethylene glycol, followed by separation of the ethylene glycol layer from the product before the final distillation, yielded the dimethylenedioxyboranes (5) and (8). The dimethoxy-esters (6) and (9) were obtained by refluxing the dihydroxyboranes and methanol through a Soxhlet extractor containing anhydrous copper sulphate.[6,7] αα-Dideuteriobenzyldi-n-butoxyborane (7D) was prepared in a similar manner to compound (7). The required αα-dideuteriobenzyl bromide was obtained by lithium aluminium deuteride reduction of methyl benzoate followed by hydrobromination of the alcohol.

The structures of the organoboranes were, so far as possible, confirmed by ^{1}H n.m.r. (see references 2 and 8—11), by i.r. spectroscopy, by mass spectrometry, and

TABLE 1

Physical characteristics of organoboranes

Organoborane	B.p. (Torr)	Density ρ_4^{20}	Proton chemical shifts (τ) and coupling constants (J)							
			Ph	CH$_2$	(CH$_3$)	B–O	CH$_2$	CH$_2$	CH$_2$	CH$_3$
(1)	46·8 (m.p.)		2·97m	7·40s						
(2)			*b*	7·27s[b]						
(3)			2·90m	7·71s						
(4)			*b*	7·70q[b,c] J = 7·5	8·77d[b] J = 7·5					
(5)	60 (0·1)	1·0766	2·94m	7·75s			6·00s			
(6)	78 (0·35)	0·9960	2·95m	7·81s			6·51s[d]			
(7)	86 (0·15)	0·9118	2·94m	7·79s			6·22t J = 6		8·57m	9·10t J = 7
(7D)	84 (0·12)	0·9264	2·94m				6·23t J = 6		8·60m	9·12t J = 7
(8)	67 (0·5)	1·0590	2·92m	7·57q[c] J = 7·5	8·68d J = 7·5		6·03s			
(9)	40 (0·04)	0·9593	2·90m	7·62q[c] J = 7·5	8·77d J = 7·5		6·53s[d]			
(10)	76 (0·12)	0·9061	2·92m	7·64q[c] J = 7·5	8·77d J = 7·5		6·23t J = 6		8·60m	9·12t J = 7
(11)[e]	229 (m.p.)		2·88m[f]	8·10s[f]			6·33m[f]	7·21m[f]		
(12)[g]	204 (m.p.)		2·84m[f]	7·98q[c,f] J = 7·5	8·76d[f] J = 7·5		6·30m[f]	7·24m[f]		

[a] τ = 10 for Me_4Si. J in Hz. In CCl_4 unless otherwise noted. Assigned values are in agreement with data in refs. 2 and 8—11. [b] In benzene. [c] CH group. [d] CH_3 group. [e] 2-Benzyl-1,3-dioxa-2-bora-6-azabicyclo[3,3,0]octane [Found: C, 63·95; H, 7·55; N, 6·6%; M (m.s.) 205. Calc. for $C_{11}H_{16}BNO_2$; C, 64·45; H, 7·85; N, 6·85%; M, 305·08]; $\nu_{max.}$ (N–H) = 2095 cm^{-1} in Nujol and halogenocarbon oil mulls. [f] In CD_3OD. [g] 2-(1-Phenylethyl)-1,3-dioxa-2-bora-6-azabicyclo-[3,3,0]octane [Found: C, 65·9; H, 8·1; N, 6·25%; M (m.s.) 219. Calc. for $C_{12}H_{18}BNO_2$: C, 65·75; H, 8·2; N, 6·4; M, 219·10]; $\nu_{max.}$ (N–H) = 3155 cm^{-1} in Nujol and halogenocarbon oil mulls.

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[6] K. Torsell, *Progr. Boron Chem.*, 1964, **1**, 369.

[7] K. Torsell, *Acta Chem. Scand.*, 1954, **8**, 1779.

[8] A. G. Davies, D. H. Hare, and R. F. M. White, *J. Chem. Soc.*, 1960, 1040.

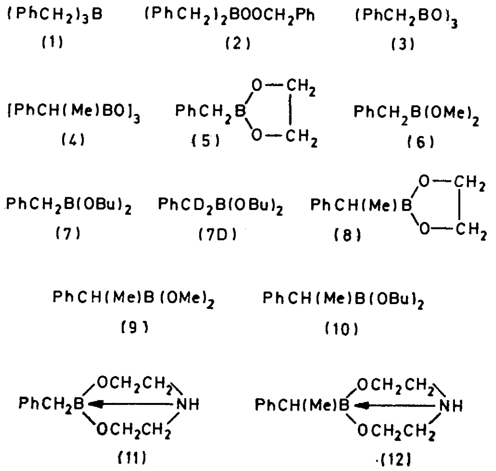
[9] J. P. Laurent, J. P. Bonnet, and G. Commenges, *Bull. Soc. chim. France*, 1967, 2702.

[10] E. F. Mooney and P. H. Winson, *Chem. Comm.*, 1967, 341.

[11] R. Heyes and J. C. Lockhart, *J. Chem. Soc.* (*A*), 1968, 326; J. C. Lockhart, *ibid.*, 1968, 869.

by chemical analyses. The boron in the organoboranes was oxidized to boric acid with 30% H_2O_2 and the boric acid was then titrated with a 0·05N-NaOH solution in the presence of mannitol with Bromothymol Blue as the indicator.[2,12] The C, H, and N analyses were carried out by Mr. J. R. H. Seguin of these laboratories.

Procedure.—The experimental apparatus and general kinetic procedure have been previously described.[1] Benzene was used as the solvent for compounds (1)—(4). The dialkoxyboranes (5)—(10) were oxidized neat or in chlorobenzene solution using di-t-butyl hyponitrite as initiator. The rates of initiation were determined during oxidation by the injection of galvinoxyl [compounds (1), (3), and (4)] or 2,6-di-t-butyl-4-methoxyphenol [compounds (5)—(10)]. All the kinetic work described in this paper was carried out at 30°.



Addition of small amounts of pyridine (100—250 mol %) reduced the rate of oxidation of tribenzylborane sufficiently for the kinetics to be studied.[1] Retardation of the reaction is due to the formation of a tribenzylborane–pyridine complex.[1] Under conditions comparable to those of the kinetic experiments the enthalpy of formation of this complex, ΔH, was measured as $-16·6 \pm 0·1$ kcal mol^{-1}

$$(PhCH_2)_3B_{soln.} + py_{soln.} \longrightarrow (PhCH_2)_3B,py_{soln.}$$

(*cf.* $-14·4$ and $-10·0$ for $Bu^n{}_3B$,py and $Bu^s{}_3B$,py, respectively [1]). Measurements were made in a simple Dewar flask calorimeter which had been previously calibrated by the neutralization of tris(hydroxymethyl)aminomethane in an excess of 0·1M-hydrochloric acid.[13]

RESULTS

(*i*) *Benzyldialkoxyboranes and* 1-*Phenylethyldialkoxyboranes* (5)—(10).—These organoboron compounds belong to Class I, as previously defined.[1] That is, they do not undergo spontaneous autoxidation at any significant rate at ambient temperatures. For kinetic studies the oxidations were initiated with di-t-butyl hyponitrite (0·05M). The reactions are strongly autocatalytic, the autocatalysis being more pronounced for the 1-phenylethyldialkoxyboranes than for the benzyldialkoxyboranes. However, the ***initial*** rates of oxidation at 30° conform to the usual kinetics. That is, the initial rates are proportional to the borane concentration, to the square root of the rate of chain initiation and are independent of oxygen pressures in the range 160—750 Torr. Mean values of $k_p/(2k_t)^{\frac{1}{2}}$ calculated from relation (1) are given in Table 2 for three

$$P_{init} = \frac{k_p[\text{Borane}]R_i^{\frac{1}{2}}}{(2k_t)^{\frac{1}{2}}} \qquad (1)$$

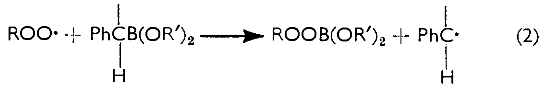
benzyldialkoxyboranes and three 1-phenylethyldialkoxyboranes.

TABLE 2

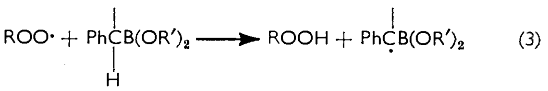
Rate constant data for the initial stages in the oxidation of dialkoxyboranes (5)—(10) at 30°

Benzyldialkoxyboranes	$k_p/(2k_t)^{\frac{1}{2}} \times 10^3$ ($l^{\frac{1}{2}}$ mol$^{-\frac{1}{2}}$ s$^{-\frac{1}{2}}$)
(5)	1·16
(6)	1·20
(7)	1·07
(7D)	0·45
1-Phenylethyldialkoxyboranes	
(8)	5·63
(9)	5·80
(10)	1·15

Kinetic studies cannot themselves distinguish between the two possible rate-controlling propagation steps (2) and (3).



$$ROO\cdot + Ph\overset{|}{\underset{H}{\underset{|}{C}}}B(OR')_2 \longrightarrow ROOB(OR')_2 + Ph\overset{|}{\underset{H}{\underset{|}{C}}}\cdot \qquad (2)$$



$$ROO\cdot + Ph\overset{|}{\underset{H}{\underset{|}{C}}}B(OR')_2 \longrightarrow ROOH + Ph\overset{|}{\dot{C}}B(OR')_2 \qquad (3)$$

For this reason, product studies were undertaken on several dialkoxyboranes. The hydroperoxide and peroxyborane might, in principle, be distinguished by an iodometric peroxide titration, by i.r. spectroscopy, or by ^1H n.m.r. spectroscopy. With an extensively oxidized sample the peroxide titre (carried out under vigorous conditions) agreed with the yield of peroxide estimated from the n.m.r. spectrum. However, as the experimental conditions for the titration were made less vigorous the titre fell but there was no obvious lower limit that could safely be taken to be hydroperoxide. I.r. spectroscopy showed a hydrogen-bonded OH group was formed during oxidation. At high conversions this appears to be due mostly to benzyl alcohol (or 1-phenylethanol) to judge from the n.m.r. spectra. The alcohol is probably formed principally in the chain-terminating step since the appropriate carbonyl compound was found in approximately equal amount, *e.g.*

$$2PhCH_2OO\cdot \longrightarrow PhCH_2OH + PhCHO + O_2$$

Quite extensive oxidation was required before ^1H n.m.r. spectroscopy could be used for the analysis. Complete oxidation of the benzyldialkoxyboranes took 5 days at 30° and required *ca.* 55 mol % of oxygen.* About 16%

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* The dimethylenedioxyboranes (5) and (8), became extremely viscous during oxidation. The dioxaboracyclopentane ring opens to yield dimeric or polymeric products (see ref. 14). The extent of ring opening for (5) (broad singlet due to OCH_2CH_2O group at τ 6·14) is approximately equivalent to the extent of borane oxidation, while for (8), only *ca.* half of the five-membered rings have opened when oxidation is complete.

[12] J. P. Dixon, 'Modern Methods in Organic Microanalysis,' Van Norstrand, London, 1968, pp. 172—183.

[13] R. J. Irving and I. Wadsö, *Acta Chem. Scand.*, 1964, **18**, 195.

[14] S. H. Shore and S. G. Rose, *Inorg. Chem.*, 1962, **1**, 744 (and later papers); A. Finch, P. J. Gardner, and E. J. Pearn, *Trans. Faraday Soc.*, 1966, **62**, 1072.

$PhCH_2OOB(OR')_2$ and 74% $PhCH_2OB(OR')_2$ were formed together with minor amounts (*ca.* 3% each) of benzyl alcohol, benzaldehyde, and bibenzyl. Similar results were obtained with the 1-phenylethyldialkoxyboranes except that oxidation was complete in *ca.* a day and the ratio $[PhCH(Me)OOB(OR')_2]/[PhCH(Me)OB(OR')_2]$ was *ca.* 1 : 1. The higher proportion of peroxide in the oxidation products of compounds (8), (9), and (10) may be due to the shorter duration of the oxidations or to steric retardation of the oxidation–reduction reaction which yields the alkoxyborane.

$$\mathrm{ROOB}{<} + \mathrm{RB}{<} \longrightarrow 2\mathrm{ROB}{<}$$

These product studies left us reasonably well satisfied that in the overall oxidation the principal rate-controlling propagation step involved peroxyl radicals in an S_H2 reaction at boron. However, the question remained as to whether this was true in the initial stages of the oxidation where the kinetic measurements were made. Now, if the *same* rate-controlling propagation and termination steps obtain throughout the oxidation, the observed autocatalysis would have to be due to an increasing rate of chain initiation. That is, as the oxidation proceeds its rate would increase because R_i increases while $k_p/(2k_t)^{\frac{1}{2}}$ would remain constant. That this is not the case is illustrated by the data in Table 3. Measurements of oxidation rates and of rates of initiation indicate that only part of the autocatalysis is due to an increase in R_i. There is also a phenomenal increase in $k_p/(2k_t)^{\frac{1}{2}}$ which must result from a profound change in the rate-controlling propagation step. However, as we have already noted, the products are consistent with reaction,

$$\mathrm{ROO}\cdot + \mathrm{RB}{<} \longrightarrow \mathrm{ROOB}{<} + \mathrm{R}\cdot$$

being the only significant propagation step. (This reaction is, of course, followed by the non-chain oxidation–reduction process which yields $\mathrm{ROB}{<}$ as a major product.)

TABLE 3

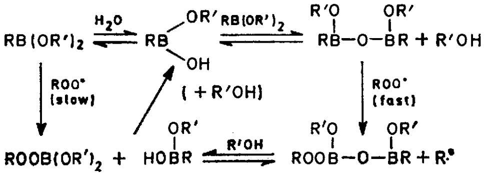
Changes in the oxidizability of some dialkoxyboranes during autoxidation at 30° [a]

Borane	[Borane] initial (M)	$[O_2]$ absorbed (M)	[Borane] remaining (M)	Oxid. rate × 10^6 (mol l^{-1} s^{-1})	R_i × 10^7 (mol l^{-1} s^{-1})	$k_p/(2k_t)^{\frac{1}{2}}$ × 10^3 ($l^{\frac{1}{2}}$ $mol^{-\frac{1}{2}}$ $s^{-\frac{1}{2}}$)
(5)	6·7	0	6·7	2·4	0·96	1·16
(5)	6·7	0·73	5·5	190	73	13
(5)	6·7	2·0	4·2	165	75	14
(5)	2·2	0	2·2	0·8	0·9	1·2
(5)	2·2	0·13	2·0	9·6	8	5·3
(5)	2·2	0·2	1·9	22	14	10
(7)	3·7	0	3·7	1·4	1·2	1·07
(7)	3·7	1·2	1·7	260	1070	15
(7)	3·7	1·3	1·5	300	1560	16
(10)	3·5	0	3·5	1·3	1·1	1·15
(10)	3·5	0·2	3·2	8·6	4·3	4·1
(10)	3·5	0·5	2·8	100	40	18
(10)	3·5	0·9	2·1	340	115	48
(10)	3·5	1·0	1·9	360	90	63

[a] Initiated with 0·05M-di-t-butyl hyponitrite, R_i measured by the induction period method using galvinoxyl or 2,6-di-t-butyl-4-methoxyphenol.

The apparent conflict between the analyses and the kinetics can be resolved if it is assumed that the alkyldialkoxyboranes become partially hydrolysed during the oxidation and that the resulting hydroxyboranes react with more alkyldialkoxyborane to form oxybisboranes (see Scheme 1). Now oxybisboranes with the structure $\mathrm{R\overset{|}{B}O\overset{|}{B}R}$ are known to oxidize very much faster than alkoxyboranes with the structure $\mathrm{R\underset{|}{B}OR'}$.[1]

As the oxidation progresses and more oxybisboranes are produced the oxidizability, $k_p/(2k_t)^{\frac{1}{2}}$, of the system will increase. However, since the oxidized oxybisborane will itself be hydrolysed, the final products will be the same as those derived from a direct oxidation (S_H2 attack at boron) of the alkyldialkoxyborane.

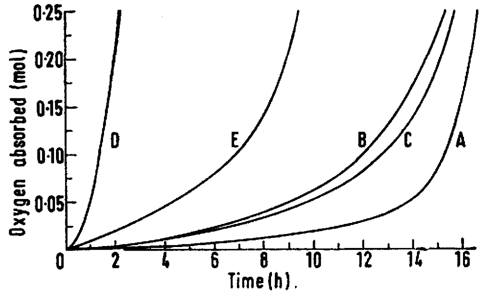


SCHEME 1

This reaction scheme implies that water should catalyse the oxidation of alkyldialkoxyboranes. That this is indeed the case is illustrated in the Figure for compound (5), and it is worth noting at this point that the oxidations of most other types of organoboron compounds are retarded by the addition of water.[1,15] The bimolecular chain-

$$2\mathrm{ROOH} \longrightarrow \mathrm{RO}\cdot + \mathrm{ROO}\cdot + \mathrm{H_2O}$$

initiating reaction may provide the water that initiates the autocatalysis. Some hydroxyborane may also be formed by an intramolecular hydrolysis.



The autoxidation of benzyldimethylenedioxyborane. (A) 6·7M-[(5)] uninitiated. (B) 6·7M-[(5)] initiated with 0·05M-t-butyl hyponitrite; (C) 6·7M-[(5)] plus 0·1M-$[H_2O]$; (D) 6·0M-[(5)] plus 5·6M-$[H_2O]$; (E) 6·7M-[(5)] plus 0·1M-[t-BuOOH]

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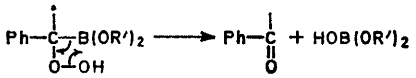
[15] A. G. Davies, *Progr. Boron Chemistry*, 1964, **1**, 265.



Since the question as to whether the *initial* rates of oxidation corresponded to peroxyl radical attack at boron or at hydrogen remained unanswered a sample of αα-dideuteriobenzyldi-n-butoxyborane (7D) was prepared. By analogy with hydrocarbon autoxidations,[16] abstraction of the deuterium should occur at *ca.* 5—10% of the rate at which hydrogen would be abstracted from (7). On the other hand, an S_H2 reaction at boron would occur at very similar rates in (7) and (7D). In the initial stages of the oxidation the value of $k_p/(2k_t)^{\frac{1}{2}}$ for (7D) was $0{\cdot}45 \times 10^{-3}$ $l^{\frac{1}{2}}$ $mol^{-\frac{1}{2}}$ $s^{-\frac{1}{2}}$ when this compound was oxidized under conditions as similar as possible to those for which (7) yields $k_p/(2k_t)^{\frac{1}{2}} = 1{\cdot}07 \times 10^{-3}$ $l^{\frac{1}{2}}$ $mol^{-\frac{1}{2}}$ $s^{-\frac{1}{2}}$. The resultant deuterium isotope effect, k_H/k_D, of 2·4 is too large to be a secondary effect. Therefore, in the initial stages of the oxidation of compound (7) substitution at boron is much less important than abstraction of the benzylic hydrogen.

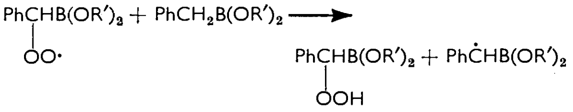
TABLE 4

Rate constant data for the oxidation of tribenzylboroxine (3) and tri-(1-phenylethyl)boroxine (4) at 30° [a]

$[3] \times 10^4$ (M)	$P \times 10^5$ (mol l^{-1} s^{-1})	$R_i \times 10^7$ (mol l^{-1} s^{-1})	$P/[(3)]R_i^{\frac{1}{2}}$ ($l^{\frac{1}{2}}$ $mol^{-\frac{1}{2}}$ $s^{-\frac{1}{2}}$)	$[(4)] \times 10^4$ (M)	$P \times 10^5$ (mol l^{-1} s^{-1})	$R_i \times 10^7$ (mol l^{-1} s^{-1})	$P/[(4)]R_i^{\frac{1}{2}}$ ($l^{\frac{1}{2}}$ $mol^{-\frac{1}{2}}$ $s^{-\frac{1}{2}}$)
6·3	0·45	0·046	106	1·6	0·64	0·021	850
25	2·8	0·47	52	1·7	0·75 [b]	0·026	850
25	2·4	0·49	42	6·2	9·0	0·31	830
49	19	3·3	67	11	16	0·67	580
49	19 [b]	3·3	67	11	32 [b]	0·83	960
50	18	3·7	60	12	34	1·0	910
73	54	8·8	79	13	38	1·0	930
75	34	7·8	51	23	110	4·0	760
86	43	4·0	79	23	110	3·1	860
88	38	4·7	63	27	220	7·7	920
130	79	15	50	36	400	11	1050
240	500	98	66	40	400	18	750
600	1770	190	68				
700	1260	160	45				

[a] At 750 Torr O_2 unless otherwise noted. [b] At 160 Torr O_2.

The rate constant for what must be the principal initial propagation reaction (4) can be estimated to be *ca.* 5



$$PhCH(OO\cdot)B(OR')_2 + PhCH_2B(OR')_2 \longrightarrow PhCH(OOH)B(OR')_2 + Ph\dot{C}HB(OR')_2 \qquad (4)$$

l mol^{-1} s^{-1} if it is assumed that this secondary peroxyl radical has a termination rate constant which lies in the usual range for such radicals (*viz.*, *ca.* 2×10^7 l mol^{-1} s^{-1} refs. 17 and 18). Such a rate constant is of the magnitude expected for the abstraction of a benzylic hydrogen.[18] Some additional activation of this hydrogen by the adjacent boron would also be expected.[19-23]

Because the isotope effect calculated from the rates of oxidation of compounds (7) and (7D) is rather smaller than might be expected for a hydrogen abstraction by a peroxyl radical there is a possibility that (7D) is oxidized principally *via* an attack at boron, the abstraction of deuterium making a negligible contribution to the overall rate. Although this possibility cannot be checked it does allow us to put an *upper* limit on the rate constant for the hypothetical propagation reaction (5). That is, the rate constant for

$$PhCD_2OO\cdot + PhCD_2B(OR')_2 \longrightarrow PhCD_2OOB(OR')_2 + PhCD_2\cdot \qquad (5)$$

the self-reaction of benzylperoxyl radicals at 30° is 3×10^8 l mol^{-1} s^{-1} (ref. 17) and hence, for the $PhCD_2OO\cdot$ radical $2k_t = (1/1{\cdot}37) \times 3 \times 10^8 = 2{\cdot}2 \times 10^8$ l mol^{-1} s^{-1}.[24] Combined with $k_p/(2k_t)^{\frac{1}{2}} = 0{\cdot}45 \times 10^{-3}$ this yields an upper limit for k_p of 5 l mol^{-1} s^{-1} for the S_H2 reaction at boron.

Since an 1-deuterio-1-phenylethyldialkoxyborane was not examined a firm distinction between hydrogen abstraction and substitution at boron in the initial stages of the oxidation of compounds (8), (9), or (10) is not possible. However, there seems no reason to suppose that the stabilizing influence of the α-methyl group would strongly favour one process over the other. By analogy, therefore, hydrogen abstraction should predominate in the early stages of the oxidation with propagation rate constants probably in the range 0·1—1·0 l mol^{-1} s^{-1}.*

(*ii*) *Tribenzylboroxine* (3) *and Tri-*(1-*phenylethyl*)*boroxine* (4).—These two compounds absorb *ca.* 2 mol O_2 per mol of boroxine. They belong to the previously defined [1] Class II of organoboranes since their self-initiated oxidation is extremely rapid. These oxidations are, in fact, only just under kinetic control in our apparatus.

Oxidation could be stopped in mid-course by the injection of galvinoxyl and the kinetics indicate a rate-controlling substitution of an alkylperoxyl radical for an alkyl radical at the boron centre (see Table 4). For compound (3)

$$ROO\cdot + (RBO)_3 \longrightarrow ROO(R_2)(BO)_3 + R\cdot$$

the mean value of $k_p/(2k_t)^{\frac{1}{2}}$ is 64 $l^{\frac{1}{2}}$ $mol^{-\frac{1}{2}}$ $s^{-\frac{1}{2}}$ and since $2k_t$

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* We have previously [19] estimated propagation rate constants for compounds (5)—(10) on the incorrect assumption that oxidation involved an S_H2 reaction at boron.

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$= 3 \times 10^8$ l mol^{-1} s^{-1} for the benzylperoxyl radical,[17] $k_p = 1{\cdot}1 \times 10^6$ l mol^{-1} s^{-1}. For compound (4) $k_p/(2k_t)^{\frac{1}{2}} = 850$ l$^{\frac{1}{2}}$ mol$^{-\frac{1}{2}}$ s$^{-\frac{1}{2}}$, $2k_t = 2{\cdot}5 \times 10^7$ l mol^{-1} s^{-1} for the 1-phenylethylperoxyl radical,* $k_p = 4{\cdot}3 \times 10^6$ l mol^{-1} s^{-1}.

(iii) *Tribenzylborane*, (1).—The oxidation of tribenzylborane is diffusion-controlled and occurs without any observable induction period as we would expect for a trialkylborane.[1] Oxidation of 0·1M-solutions of (1) could be inhibited by galvinoxyl,[1] or iodine.[26,27] Although iodine is a more efficient inhibitor than galvinoxyl on a molar basis it is of much less value for kinetic studies since the induction periods are not linearly related to the iodine concentration. Instead, the induction periods increase rapidly as the iodine concentration increases. While this might result from interference by iodine with the initiation process, studies on iodine-inhibited hydrocarbon oxidations suggest [28] that the iodine is regenerated after the initial inhibition step (trapping of an alkyl radical).

As has been found with other trialkylboranes,[1] the oxidation of compound (1) is strongly retarded by pyridine which associates with the borane to form an unreactive

$$(PhCH_2)_3B + py \rightleftharpoons (PhCH_2)_3B,py$$

borane–pyridine complex. The pyridine-retarded oxidation is slow which indicates that it is not diffusion controlled. Furthermore, the reaction can be inhibited with galvinoxyl. The kinetics of the retarded oxidation of compound (1) are identical to those observed in similar systems [1] and they imply that oxidation involves only the presence of small amounts of free compound (1) in equilibrium with the complex. The kinetic equation is

$$\frac{\mathrm{P[py]}}{[(1)]_0 R_i^{\frac{1}{2}}} = \frac{k_p}{(2k_t)^{\frac{1}{2}} K}$$

where $K = [(1,\text{py})]/[(1)][\text{py}]$, k_p refers to the reaction of benzylperoxyl radicals with uncomplexed borane, and $[(1)]_0$ is the total concentration (complexed and uncomplexed) of borane in the solution. Data in support of this equation are given in Table 5. The mean value of $k_p/(2k_t)^{\frac{1}{2}}K$ is $3{\cdot}4 \times 10^{-2}$ mol$^{\frac{1}{2}}$ l$^{-\frac{1}{2}}$ s$^{-\frac{1}{2}}$ at 30°.

Since we have not yet developed a method for measuring K directly, it was estimated from the van't Hoff relation

$$\log_{10} K = \frac{\Delta S}{2{\cdot}3} - \frac{\Delta H}{2{\cdot}3RT}$$

by the method previously employed.[1] That is, ΔS was taken to be $-36{\cdot}8$ cal mol^{-1} K^{-1} and ΔH, the heat of complex formation, was measured and found to be $-16{\cdot}6$ kcal mol^{-1}. This yields $K = 8{\cdot}7 \times 10^3$ l mol^{-1} at 30° and hence $k_p/(2k_t)^{\frac{1}{2}} = 3 \times 10^2$ l$^{\frac{1}{2}}$ mol$^{-\frac{1}{2}}$ s$^{-\frac{1}{2}}$, combined with $2k_t = 3 \times 10^8$ l mol^{-1} s^{-1} (ref 17) this gives $k_p = 5 \times 10^6$ l mol^{-1} s^{-1} for the reaction,

$$PhCH_2OO\cdot + (PhCH_2)_3B \longrightarrow PhCH_2OOB(CH_2Ph)_2 + Ph\dot{C}H_2$$

We have previously studied the kinetics and measured propagation rate constants for the oxidation of two butylperoxydibutylboranes by injecting galvinoxyl into the oxidizing tributylborane after it had absorbed just over 1 mol. equiv. of oxygen.[1] An attempt to do the same with tribenzylborane was not very successful because there is no distinct second stage to the oxidation and because, the overall oxidation is complete in an extremely short time. Preliminary measurements suggesting that k_p for compound (2) was *ca.* 1×10^6 l mol^{-1} s^{-1} have been reported.[19] However, after more detailed study we have concluded that the oxidation of compound (2) is insufficiently distinct from the oxidation of compound (1) for meaningful rate constants to be derived.

TABLE 5

Rate constant data for the self-initiated oxidation of of tribenzylborane in pyridine–benzene at 30°

$[R_3B]$ (M) $\times 10^2$	[Pyridine] [a] (M) $\times 10^2$	$R_i \times 10^6$ (mol l^{-1} s^{-1})	$P \times 10^5$ (mol l^{-1} s^{-1})	$\frac{P[\text{py}]}{[R_3B]R_i^{\frac{1}{2}}} \times 10^2$ (mol$^{\frac{1}{2}}$ l$^{-\frac{1}{2}}$ s$^{-\frac{1}{2}}$)
1·3	1·3	2·1	6·0	4·1
1·3	1·3	2·3	5·5	3·6
1·3	2·7	0·66	0·98	2·4
2·7	2·7	3·3	8·3	4·5
7·0	7·2	1·6	4·9	3·9
7·0 [b]	7·2	1·3	4·2	3·7
7·0	7·2	1·7	5·5	4·3
7·0 [b]	7·2	2·4	6·1	4·1
7·0	7·2	3·1	4·5	2·6
7·0	12·2	0·85	1·8	3·3
7·0	12·2	0·88	1·4	2·6
7·0	18·4	0·77	0·90	2·7
13·9	14·3	4·1	7·1	3·6
13·9	36·8	0·79	0·83	2·5

[a] Oxidation stopped completely at a mol ratio $\frac{[R_3B]}{[\text{py}]}$ of $\frac{1}{3}$.

[b] At 160 Torr O_2. Other runs are at 750 Torr O_2.

DISCUSSION

Our present results and our earlier work [1] yield the following picture for the oxidation of alkyldialkoxyboranes. Peroxyl radicals (and t-butoxyl radicals [19,20,29]) either do not attack the pure compounds at boron or else such attack is very slow. This is the case even when the alkyl radical that would be displaced is resonance stabilized. The low reactivity of the boron atom may well be due to the known intermolecular association of such esters *via* boron–oxygen bridges.[9,10] Instead of attacking boron the peroxyl radicals prefer to abstract hydrogen from the carbon atom adjacent to the boron and, perhaps, from the ester groups. As a consequence, compounds containing hydroxy-groups are produced and these promote the formation of oxybisboranes with the structure $R(R'O)BOB\!<$. Such compounds are attacked at boron by peroxyl radicals and are oxidized much more readily than the starting $RB(OR')_2$. The oxidation is therefore autocatalytic but the principal products are, nevertheless, those which would have been formed if the starting compound had indeed suffered an S_H2 process at boron, *i.e.* $ROOB(OR')_2$ and $ROB(OR')_2$.

Tribenzylborane and the boroxines (3) and (4) behave

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* Recently redetermined,[25] our first value for this rate constant was 4×10^7 l mol^{-1} s^{-1}.[17]

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TABLE 6

Comparison of rate constants for the autoxidation of some organoboranes

R	Rate constant[a] (l mol^{-1} s^{-1}) $(RBO)_3$	 R_3B
n-Butyl	1×10^3	2×10^6
s-Butyl	5×10^4	8×10^4
t-Butyl	3×10^4	
Benzyl	1×10^6	5×10^6
1-Phenylethyl	4×10^6	

[a] The rate constants are given per mol of borane and have not been statistically corrected for the number of equivalent R groups available for substitution.

'normally'. That is, oxidation is rapid and occurs *via* a free-radical chain with a rate-controlling S_H2 reaction of a peroxyl radical at boron. The rate

$$\mathrm{ROO\cdot + RB}< \longrightarrow \mathrm{ROOB}< + \mathrm{R\cdot}$$

constants for these S_H2 processes are considerably greater than those found previously for the oxidation of structurally related butylboranes[1] (see Table 6). This presumably reflects the increased stability of the displaced alkyl radical.

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