207. *Peroxides of Elements Other than Carbon. Part IX.*[1] *The Course of the Autoxidation of Tris-2-methylpentylboron and Tri-n-butylboron.*

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The reduced reactivity of tris-2-methylpentylboron and of tri-n-butylboron towards oxygen may be due to inhibition of the reaction by the product. We have not been able to confirm the report that the reaction proceeds through an intermediate molecular complex.

In dilute solution, di-isobutyl-t-butylboron,[2,3] tri-s-butylboron,[4] and tri-isobutylboron [5] react with 2 mol. of oxygen to give the diperoxyboronic esters (I). In the absence of a solvent, the boronic ester (II) is usually the principal product, and is presumably formed by the reduction of an RO·OB group by an RB group.

$$\text{(I) } RB(O{\cdot}OR)_2 \xleftarrow{2O_2,\ \text{soln.}} R_3B \xrightarrow{O_2,\ \text{neat}} RB(OR)_2 \text{ (II)}$$

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[1] Part VIII, Alleston and Davies, *J.*, 1962, 2465.
[2] Part III, Abraham and Davies, *J.*, 1959, 429.
[3] Part VII, Davies, Hare, and White, *J.*, 1961, 341.
[4] Part IV, Davies and Hare, *J.*, 1959, 438.
[5] Davies, Hare, and White, *J.*, 1960, 1040.

We have now investigated the autoxidation of tris-2-methylpentylboron and tri-n-butylboron because preliminary work in these and other laboratories had suggested that these compounds in solution reacted with less than 2 mol. of oxygen. We hoped that these deviations from normal behaviour might throw light on the mechanism of the autoxidation.

When air was admitted slowly to tris-2-methylpentylboron, the boronate (II) was formed, and this gave 2-methylpentanol and 2-methylpentylboronic acid on hydrolysis. In solvents, particularly in ethers, this trialkylboron absorbed oxygen more slowly than others which we have investigated.[2-5] Up to 1·8 mol. of oxygen were taken up, giving up to 1·74 mol. of peroxide (see Table). After a longer period in diethyl ether, a product containing 1·88 mol. of peroxide was obtained. The peroxide was reduced, over platinum, by 97% of the calculated amount of hydrogen, giving the corresponding alcohol and boronic acid.

Autoxidation of trialkylborons.

THF = tetrahydrofuran; C_6H_{12} = cyclohexane; C_8H_{18} = " iso-octane."

Solvent	Volume (c.c.)	BR_3 (g.)	Time (min.)	O_2 absorbed (mol.)	Peroxide formed (mol.)
		Tri-2-methylpentylboron			
Et_2O	75	0·1273	48	0·95	—
Et_2O	40	0·1999	180	1·06	—
			1000	—	1·88
Dioxan	75	0·1212	88	0·97	—
THF	50	0·1408	59	1·23	—
PhOMe	30	0·1383	180	1·80	1·61
$MeNO_2$	30	0·2154	150	1·73	1·60
C_6H_{12}	30	0·1844	180	1·41	1·17
C_6H_{12}	30	0·3102	180	1·79	1·63
C_6H_6	30	0·3119	110	1·80	1·74
		Tri-n-butylboron			
Bu_2O	50	0·4174	55	0·90	0·19
Bu_2O	50	0·1993	45	1·31	0·54
PhOMe	200	0·5007	38	1·66	1·36
C_6H_{12}	50	0·3864	46	1·63	1·61
C_6H_{12}	50	0·2786	85	1·64	1·64
C_6H_{12}	65	0·2152	60	1·83	1·80
C_8H_{18}	50	0·2676	55	1·78	1·70
C_8H_{18}	50	0·3762	45	1·59	1·19
C_6H_6	200	0·4279	60	1·67	—

In our experiments with tri-n-butylboron,[2] before the nature of the autoxidation was fully appreciated, the maximum uptake of oxygen recorded was 1·2 mol., and other workers [6-8] have reported a similar restricted reactivity. The results of our re-investigation of this reaction are given in the Table. Again the reaction was rather slow. In all solvents except di-n-butyl ether, 1·5—1·8 mol. of oxygen were absorbed and substantially all of this was present as peroxide in the product.

The incomplete formation of the diperoxyboronate (I) is thus apparently real, and cannot be the result of some reduction to, for example, the boronate (II), because an uptake of $(2 - n)$ mol. of oxygen would then give only $(2 - 2n)$ mol. of peroxide. It also cannot represent the position of an equilibrium because the reaction shows no sign of being reversible.

It is most likely that the product can inhibit the autoxidation of the reactant without itself undergoing any chemical change. We have suggested earlier [2,3] that the autoxidation involves nucleophilic attack of oxygen at boron, accompanied or followed by a nucleophilic 1,3-rearrangement of the alkyl group from boron to oxygen (eqn. 1).

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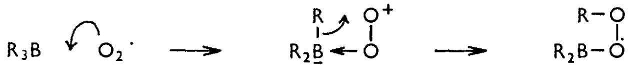
[6] Bawn, Margerison, and Richardson, *Proc. Chem. Soc.*, 1959, 397.
[7] Zutty and Welch, *J. Org. Chem.*, 1960, **25**, 861.
[8] Nakayama, Tsuruta, and Furukawa, *Makromol. Chem.*, 1960, **40**, 79.



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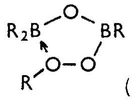
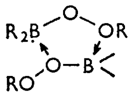
Lewis bases such as amines or water inhibit the autoxidation by co-ordinating to the boron and preventing the oxygen's attack. A peroxidic product of oxidation might serve as the inhibiting ligand, and we suggested[4] that this effect, operating intramolecularly in the structure (III), accounted for the fact that s-butylborinic anhydride reacted with only 1 mol. of oxygen to give a monoperoxide. In the present case the peroxide (I) might exert a similar effect intermolecularly (*e.g.*, IV) and it is reasonable that this should be most pronounced in a tri-n-alkylboron where the steric hindrance towards association would be least.

Proof that a peroxide can act as an inhibitor was obtained by autoxidation in the presence of di-t-butyl peroxide, the rate of uptake of oxygen being drastically reduced.

Zutty and Welch[7] have presented evidence that in the autoxidation of tri-n-butylboron, the two processes shown in equation (1) can be observed as separate and distinct steps. A molar equivalent of oxygen was rapidly passed through the dilute solution of the trialkylboron. Dissolved oxygen was then swept out with nitrogen, and aliquot portions of the solution were analysed periodically for peroxide. The peroxide content increased by a factor of almost three during 200 min., suggesting the initial and rapid formation of a non-peroxidic compound R_3B,O_2, followed by the slower rearrangement of this complex to the peroxide.



(III)



(IV)

We could not observe this slow build-up of titratable peroxide. If we allowed hydrocarbon solutions of tri-n-butylboron to absorb a deficiency of oxygen, the peroxide content thereafter *fell* slightly during 3—4 hr., presumably because of the reaction between RB and RO·OB groups. If an excess of oxygen had been admitted, the product at zero time was largely the diperoxide (I), and no change in peroxide content was observed during some hours.

Our results therefore contradict those of Zutty and Welch for reasons which are not clear. One possible source of difference is that the iodometric analysis of some types of organic peroxide is dependent on the presence of traces of metal ions.* It is feasible that the estimation of a complex R_3B,O_2 could similarly give irreproducible results depending on the absence or presence of unidentified catalysts.

EXPERIMENTAL

The technique for the autoxidation reactions and for the iodometric analysis of the product has been described previously.[2-5] The results are summarised in the Table.

Tris-2-methylpentylboron.—This was obtained from the hydroboration of 2-methylpent-1-ene, and was fractionally distilled at 124°/3 mm. (Found: B, 3·9. $C_{18}H_{39}B$ requires B, 4·1%).

Autoxidation Neat.—The trialkylboron (3 g.) in a loosely-stoppered bottle was allowed to react with dry air for 11 days, giving impure bis-2-methylpentyl 2-methylpentylboronate (Found: C, 69·7; H, 12·6. Calc. for $C_{18}H_{39}BO_2$: C, 72·5; H, 13·1%). This was mixed with water and fractionally distilled giving a water–2-methylpentanol azeotrope in which the alcohol was identified by gas–liquid chromatography. The residue in the distilling flask was cooled to 0°, and crystals of 2-*methylpentylboronic acid* separated, m. p. 78° (Found: C, 54·4; H, 11·0. $C_6H_{15}BO_2$ requires C, 55·4; H, 11·5%).

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* For example, Silbert and Swern[9] found that peroxy-esters could be estimated by the usual iodometric method only if the acetic acid used contained ferric ions. We are grateful to Dr. Swern for pointing out the possible relevance of this to our results.

[9] Silbert and Swern, *Analyt. Chem.*, 1958, **30**, 385.

Autoxidation in Solution.—A solution of tris-2-methylpentylboron (0·3119 g.) in benzene (*ca.* 30 c.c.) absorbed 1·80 mol. of oxygen at the gas burette. Platinum oxide (*ca.* 0·02 g.) was then added, and the solution absorbed 1·74 mol. of hydrogen (97% of theory). The mixture was filtered, the benzene removed under reduced pressure, and water added to the residue. The upper layer was 2-methylpentanol, identified by gas–liquid chromatography; the lower layer yielded crystals of 2-methylpentylboronic acid, m. p. 79°.

Tri-n-butylboron.—This was kindly given to us by Professor C. E. H. Bawn and Dr. D. Margerison of Liverpool University, and was redistilled, b. p. 79—80°/6 mm.

Inhibition of Autoxidation by Di-t-butyl Peroxide.—A mixture of tri-n-butylboron (0·1449 g.) and hydroperoxide-free di-t-butyl peroxide (1·2 g.) in cyclohexane (50 c.c.) absorbed oxygen very slowly (less than 2 c.c. after 90 min., giving $\not>$0·1 mol. of peroxide), but 1·65 mol. of peroxide had been formed after 24 hr.

Irreversibility of Autoxidation.—Tri-n-butylboron (0·2022 g.) in cyclohexane (50 c.c.) absorbed 1·61 mol. of oxygen during 73 min.; the product contained 1·48 mol. of peroxide. Nitrogen was passed through the solution for 5 hr., after which 1·40 mol. of peroxide were present; oxygen was then passed for 3 hr. and 1·40 mol. of peroxide remained. We conclude that the formation of the peroxide is irreversible under these conditions.

Attempts to Detect an Intermediate.—(*a*) (*cf.* ref. 7.) Oxygen (1·5 mol.) was passed through a sintered-glass distributor into a solution of tri-n-butylboron (0·7062 g.) in cyclohexane (60 c.c.) during 3 min. The oxygen was flushed out with dry nitrogen for 2 min., and then aliquot portions were withdrawn under nitrogen and analysed iodometrically (time after end of oxidation, peroxide content): 15 min., 0·38 mol.; 120 min., 0·30 mol.; 200 min., 0·23 mol.

(*b*) The following modified conditions were suggested to us by Dr. N. L. Zutty. Tri-n-butylboron (0·2152 g.) in cyclohexane (65 c.c.) was stirred under an excess of oxygen at room temperature at the gas burette. The uptake of oxygen was virtually complete after 40—45 min., and 1·83 mol. of oxygen had been absorbed after 1 hr. Nitrogen was then passed through the solution for 20 min. The product contained 1·80 mol. of peroxide, and this value was unchanged after 30 min. and 80 min.

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