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# Peroxides of Elements other than Carbon. Part XI.<sup>1</sup> The Autoxidation of Some Trialkylboroxines

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Trialkylboroxines in solution react with oxygen to give organoperoxyboron compounds. Tri-t-butylboroxine gives tri-t-butylperoxyboroxine in good yield. With tri-s-butylboroxine the reaction proceeds to about 80% completion, and with tri-n-butylboroxine a maximum of only about two thirds of the theoretical amount of oxygen is absorbed. The mechanism of the oxidation is discussed, and it is pointed out that the evidence does not exclude the possibility of a free-radical process.

In dilute solution, trialkylboranes react with oxygen and ROOB groups; the probable mechanism of to give the peroxyboranes (I) and (II).<sup>2</sup> The yields of the intramolecular reaction is

$$R_{3}B \xrightarrow{\mathbf{O}_{2}} R_{2}B \cdot O \cdot OR \xrightarrow{\mathbf{O}_{2}} RB(O \cdot OR)_{2}$$
(1)  
(I)

peroxide may be reduced by an intramolecular or intermolecular redox reaction between the RB

<sup>1</sup> Part X, A. G. Davies and C. D. Hall, J. Chem. Soc., 1963, 1192. <sup>2</sup> A. G. Davies, Progr. Boron Chem., 1964, **1**, ch. 6.

$$-B \xrightarrow{R} O \longrightarrow -B \xrightarrow{OR} (2)$$

The intermolecular reaction can be suppressed by carrying out the autoxidation on dilute solutions. The intramolecular reaction would be precluded with the trialkylboroxines [boronic anhydrides, (RBO)<sub>3</sub>], when

# J. Chem. Soc. (C), 1966

the peroxide would not carry a geminal alkyl group, and which might therefore provide a simpler system for investigation.

Very little work has been reported in this field. Grummitt<sup>3</sup> studied the uptake of dry oxygen by various trialkylboroxines in the absence of a solvent. The times (minutes) for samples of 0.2-0.3 g. to absorb 2 c.c. of oxygen at 25°, as R was varied, were Et 33, Pr<sup>n</sup> 36, Bu<sup>n</sup> 71, n-C<sub>6</sub>H<sub>13</sub> 105, Bu<sup>s</sup> 3, Bu<sup>t</sup> 2. Tri-n-butylboroxine absorbed 1.5 moles of oxygen per mole. The product was shown to be principally the corresponding trialkoxyboroxine (RO·BO)<sub>3</sub>,\* but an intermediate was

oxygen and the amount of peroxide formed were less. The highest peroxide yield (84%) was again obtained in nitromethane solution. With all the solvents used, a small amount of a solid separated during the autoxidation, and in cyclohexane this increased slightly during 1 week as the peroxide decomposed. The yield of solid was highest from the reaction in octane; it was separated, shown to have a negligible peroxide content, and identified by its infrared spectrum as orthoboric acid.

Tri-n-butylboroxine was autoxidised much more slowly. A maximum of  $2 \cdot 10$  mol. of oxygen were take

		The au	toxidation of	f trialkylbo	roxines			
Solvent	Volume (c.c.)	(RBO) <b>3</b> (g.)	Time Tri-t-buty	t/3 ª (min.) Vlboroxine	Oxygen absorbed mol.)	Peroxide formed (mol.)	Peroxide content after time elapsed [mol. (days)]	
None		0.2956	7 days			0.38		
С.Н.	50	0.1990	160 min	17	2.73	2.72	2.28(1)	1.10(7)
С.Н.	25	0.2575	150 1111.		2.67		2 20(1)	1 10(.)
$C_{1}H_{1}$	50	0.2100	200	17	2.71	2.68	2.44(3)	2.38(16)
$M_{eNO}$ .	50	0.2018	200	33	2.81	2.78	2.73(1)	$2 \cdot 27(14)$
MeNO <sub>2</sub>	75	0.5015	180	60		2.72	(1)	(-+)
			Tri-s-buty	lboroxine				
C.H.	50	0.2213	190 min	26	2.52	2.43	2.14(2)	1.74(7)
С.Н.,	50	0.2390	150 mm.	10	2.34	2.13	$\tilde{1} \cdot \tilde{1} \cdot \tilde{3} \cdot \tilde{2}$	0.63(7)
MeNO.	50	0.3116	250	35	2.59	2.51	$2 \cdot 14(2)$	1.90(10)
PhMe	$50^{\circ}$	0.5714	210	24	$\frac{2}{2}.54$	2.08	1.07(3)	1 00(10)
Bu <sub>o</sub> O	50	0.3675	300	- 8	2.56	2.33	2.62(2)	2.14(7)
n-C.H.,	50	0.3716	200	4 ¢	2.41	2.22 ª	$2 \cdot 22(1)$	$2 \cdot 17(3)$
$C_6 H_{11}^{11} Me$	50	0.2429	200	7	2.38	2.07	2.19(1)	1.23(20)
			Tri-n-but	ylboroxine				
C.H.	50	0.2660	23 hr.	280 *	1.69	1.51	0.78(2)	0.33(14)
PhBr	50	0.3999	$\frac{1}{27}$	280	1.91	1.13	0.93(1)	0.58(6)
MeNO.	50	0.2548	25	380	2.10	1.85	1.77(1)	1.56(6)
C.H., Me	50	0.3245	$\frac{1}{47}$		1.57	1.23	0.64(14)	(-)
C.H.,Me	50	0.6294	33		1.47	$1.25^{f}$	$1 \cdot 12(1)$	0.70(6)
n-C.H.,	70	0.8222	26		1.50	1.38	\-/	(-/
None		0.3144	7		1.29	0.62		
None		0.4243	<b>74</b>		1.57	0.26		

<sup>*a*</sup> t/3 is the time for the absorption of  $0.5 \longrightarrow 1.5$  mol. of oxygen, determined from a graph of oxygen absorption against time. <sup>*b*</sup> Oxygen was dispersed into the solution through a sintered glass plate. <sup>*c*</sup>  $0 \longrightarrow 2.0$  mol. of O<sub>2</sub> were absorbed in 11 min. <sup>*d*</sup> 2.20 mol. by hydrogenolysis. <sup>*c*</sup>  $0.2 \longrightarrow 1.2$  mol. of O<sub>2</sub>. <sup>*f*</sup> 1.30 mol. by hydrogenolysis.

detected which liberated iodine from acidified potassium iodide and catalysed the polymerisation of vinyl acetate.

We have investigated the autoxidation of tri-n-, -s-, and -t-butylboroxine, and of trimethylboroxine, in dilute solution. The results are summarised in the Table.

In dilute solution, tri-t-butylboroxine absorbed almost 3 mol. of oxygen, essentially all of which appeared in the product as peroxide. The best example was the reaction in nitromethane solution, which gave a 93%yield (on boroxine) of the triperoxide, presumably (RO·O·BO)<sub>3</sub>. The rate of decomposition of the peroxide at room temperature is shown in the Table. With all the solvents used, the solutions remained homogeneous throughout the formation and decomposition of the peroxide.

Tri-s-butylboroxine reacted at approximately the same rate as tri-t-butylboroxine, but the uptake of up (again in nitromethane), giving 1.85 mol. of peroxide A small amount of solid separated during the autoxidation in all solvents except nitromethane, and increased as the peroxide slowly decomposed.

Trimethylboroxine was inert to oxygen under the same conditions.

The correlation between oxygen absorbed and peroxide formed with these boroxines is no better than with the trialkylboranes, despite the fact that the intramolecular redox reaction (2) is now ruled out.

The peroxides derived from all three butylboroxines catalysed the polymerisation of acrylonitrile at  $25^{\circ}$  in solvents such as octane, benzene, and nitromethane.

### DISCUSSION

The mechanism that has usually been accepted for the autoxidation of alkylboranes<sup>2</sup> (and of other organo-

<sup>3</sup> O. Grummitt, J. Amer. Chem. Soc., 1942, **64**, 1811. <sup>4</sup> J. Goubeau and H. Keller, Z. anorg. Chem., 1951, **267**, 1; 1953, 272, 303.

<sup>\*</sup> Formulated by Grummitt <sup>3</sup> as being monomeric, but now known to be the cyclic trimer.4

1495

metallic compounds 5) involves nucleophilic attack of oxygen on the metal, accompanied or followed by a nucleophilic 1,3-rearrangement of the alkyl group from the metal to oxygen. The items of evidence on which

this picture is based are briefly as follows. (i) The autoxidation of tributylborane<sup>6</sup> and of tributylboroxine<sup>3</sup> is not inhibited by quinol, or that of triethylborane by iodine or methyl methacrylate.<sup>7</sup> (ii) Intermolecular or intramolecular donation of electrons into the vacant orbital of boron reduces the reactivity of the RB group. (iii) In the autoxidation of di-isobutyl-t-butylborane, the t-butyl group is more reactive than the isobutyl group.<sup>8</sup>

The results reported here are broadly compatible with this picture. The reactivity sequence in the trialkylboroxines,  $Me \ll Bu^n < Bu^s < Bu^t$ , is the same as that observed by Minato, Ware, and Traylor<sup>9</sup> in the oxidation of the boronic acids with hydrogen peroxide, where they suggested that a purely  $S_{\rm E}2$  process was involved, comparable with the second stage of reaction (3). This sequence also does not conflict with that observed in the autoxidation of di-isobutyl-t-butylborane, where primary and tertiary alkyl groups are now in intramolecular competition for oxygen.

The lower reactivity of trimethylboroxine towards oxygen has a parallel in other methylmetallic compounds (e.g., Me<sub>2</sub>Cd,<sup>10</sup> Me<sub>3</sub>B,<sup>11</sup> and Me<sub>3</sub>Al<sup>1</sup>). The nuclear quadrupole resonance spectrum of trimethylborane provides strong evidence that the methyl group hyperconjugatively releases electrons to the boron atom, and that this effect decreases as the number of  $\alpha$ -hydrogen atoms decreases; <sup>12</sup> similarly, the Lewis acidity of trimethylborane is less than that of the higher alkylboranes.13 The inertness towards oxygen may therefore be included under item (ii) above.

The relative reactivities towards oxygen reported here correlate remarkably well with those obtained by Grummitt from the reactions of the neat boroxines,<sup>3</sup> where problems of the rate of diffusion of oxygen, and of interaction of the product and the reactant, might be expected to obscure the fundamental reactivity.

Two facts, namely, that some boric acid is formed during the autoxidation, and that a non-integral number of mol. of oxygen are sometimes absorbed, cannot readily be accommodated on the basis of the mechanism shown in (3).

It seems unlikely that the boric acid resulted from hydrolysis of the peroxide (RO•O•BO)<sub>3</sub>. All the solvents

- <sup>5</sup> A. G. Davies, "Organic Peroxides," Butterworths, London,
- 1961, p. 124.
  M. H. Abraham and A. G. Davies, J. Chem. Soc., 1959, 429.
  R. L. Hansen and R. R. Hamann, J. Phys., Chem. 1963, 67, 2868.
- 8 A. G. Davies, D. G. Hare, and R. F. M. White, J. Chem. Soc., 1961, 341.
- H. Minato, J. C. Ware, and T. G. Traylor, J., Amer. Chem. Soc., 1963, 85, 3024.

were carefully dried before use, and it would be difficult to accept that hydrolysis should occur when  $R = Bu^n$ or  $Bu^s$ , but not when  $R = Bu^t$ , even after long periods of time.

Non-integral stoicheiometry, particularly with n-butyl compounds, has been observed before in the autoxidation of trialkylboranes.<sup>14</sup> It was tentatively suggested then that the autoxidation reaction might be inhibited by the autoxidation product, and a complex of the type which was envisaged has since been isolated from the autoxidation of trimethylborane at low temperature.<sup>15</sup>

It should be recognised, however, that the evidence for the mechanism shown in (3) is not compelling, and the possibility cannot be ruled out that the reaction might follow in part, or even in whole, a free-radical route. This should be seriously considered, since recent studies on non-autoxidation systems indicate that organoboranes readily undergo free-radical displacement reactions at the boron atom.<sup>16</sup>

The item of evidence (ii) would be met equally well if the reagent which attacked the metal atom did so as a radical rather than as a formally electron-paired species. The negative evidence of item (i) might be discounted on the grounds that the chain-transfer agents which were tested were merely too inefficient relative to the borane to have any significant effect on the autoxidation, and indeed Grummitt did show that 0.1% of phenyl-2-naphthylamine inhibited the autoxidation of tri-n-butylboroxine<sup>3</sup> The order of reactivity of the alkyl groups in item (iii)  $(Bu^t > Bu^i)$  is the same as the order of stability of the two alkyl radicals, and thus presumably of their ability to act as leaving groups in homolytic displacements.

Some contribution to the reaction by a chain mechanism such as that shown in (4) and (5) thus cannot be ruled out.

$$R \cdot + O_{2} \longrightarrow RO_{2} \cdot (4)$$

$$RO_{2} \cdot + B - R \longrightarrow \left[ RO_{2} - B - R \right] \longrightarrow RO_{2}B + R \cdot (5)$$

This possibility is being investigated.

Note Added in Proof-We have now obtained evidence for this mechanism in that the antoxidation of optically active 1-phenylethylboronic acid gives the racemic peroxide, and is inhibited by galvinoxyl (A. G. Davies and B. P. Roberts, Chem. Comm., 1966, 298.).

### EXPERIMENTAL

Solvents .--- Di-n-butyl ether and the hydrocarbon solvents were dried first over calcium chloride and then over sodium wire, and distilled from sodium under nitrogen immediately

A. G. Davies and J. E. Packer, J. Chem. Soc., 1959, 3164.
 R. C. Petry and F. H. Verhoek, J. Amer. Chem. Soc., 1956,

- 78, 6416. <sup>12</sup> P. Love, J. Chem. Phys., 1963, 39, 3044. <sup>13</sup> H. C. Brown, J. Amer. Chem. Soc., 1945, 67, 374. <sup>14</sup> Dovies and D. G. Hare, J. Chem. Soc., 1965 <sup>14</sup> A. G. Davies and D. G. Hare, *J. Chem. Soc.*, 1959, 438; A. G. Davies, D. G. Hare, and O. R. Khan, *ibid.*, 1963, 1125.
- <sup>15</sup> L. Parts and J. T. Miller, *Inorg. Chem.*, 1964, 3, 1483.
   <sup>16</sup> J. Grotewold and E. A. Lissi, *Chem. Comm.*, 1965, 21;
- D. S. Matteson, J. Org. Chem., 1964, 29, 3399.

## J. Chem. Soc. (C), 1966

before use. Nitromethane was dried over calcium chloride, then distilled under nitrogen.

Chromatography of Peroxides.—Peroxides were identified by thin-layer chromatography on Merck Kieselgel G, using chloroform-ether (3:1 v/v) as eluent. The  $R_{\rm F}$  values of some common peroxides are: hydrogen peroxide 0·13, t-butyl hydroperoxide 0·62, s-butyl hydroperoxide 0·66, 1-methyl-1-phenylethyl hydroperoxide 0·72, 1,2,3,4-tetrahydro-1-naphthyl hydroperoxide 0·72, 1-phenylethyl hydroperoxide 0·76, 1-methyl-1-phenylpropyl hydroperoxide 0·78, decahydro-9-naphthyl hydroperoxide 0·79, t-butyl peroxyacetate 0·51, t-butyl peroxybenzoate 0·89, benzoyl peroxide 0·92, 1-methyl-1-phenylethyl xanthydryl peroxide 0·97. The peroxides were detected with acidified ferrous thiocyanate.<sup>17</sup>

Trialkylboroxines.—The alkylboronic acids were prepared under nitrogen by treating methyl borate with the appropriate Grignard reagent at  $-75^{\circ}$ . The isomeric butylboronic acids were dehydrated by removing water as an azeotrope with toluene, yielding tri-n-butylboroxine, b. p.  $108^{\circ}/5 \cdot 5 \text{ mm}$ . (Found: B, 12·7. Calc. for  $C_{12}H_{27}B_3O_3$ : B,  $12\cdot9_{\circ\circ}$ ), diethanolamine ester, m. p.  $152-154^{\circ}$  (lit.,<sup>18</sup> 153- $155^{\circ}$ ); tri-s-butylboroxine, b. p.  $79\cdot5-80\cdot5^{\circ}/2\cdot5$  mm. (Found: B,  $13\cdot0_{\circ\circ}$ ), diethanolamine ester, m. p.  $156^{\circ}$ (lit.,<sup>8</sup> 156°); tri-t-butylboroxine, b. p.  $67\cdot5-68^{\circ}/5\cdot5$  mm., m. p.  $29-31^{\circ}$  (lit.,<sup>19</sup> 30-31°), diethanolamine ester, m. p.

<sup>17</sup> M. H. Abraham, A. G. Davies, D. R. Llewellyn, and E. M. Thain, Analyt. Chim. Acta, 1957, 17, 499.

<sup>18</sup> S.-O. Lawesson, Arkiv Kemi, 1956, 10, 171.

246° (from acetonitrile) (Found: C, 55.5; H, 10.7. Calc. for  $C_8H_{18}BNO_2$ : C, 56.1; H, 10.6%). A sample prepared some years ago <sup>20</sup> had m. p. 248° (from acetonitrile) (Found: C, 56.3; H, 10.5%). Lawesson reported the same compound to have m. p. 220—222° (from acetone).<sup>18</sup>

Methylboronic acid was dehydrated by treating it briefly with concentrated sulphuric acid,<sup>19</sup> to give trimethylboroxine, b. p. 80° (15%); *diethanolamine ester*, m. p. 210—212° (Found: C, 47·0; H, 9·2; N, 10·8.  $C_5H_{12}BNO_2$ requires C, 46·6; H, 9·4; N, 10·9%).

Autoxidations.—The boroxines were enclosed in capsules and autoxidised at the gas burette by the usual procedure. The results are shown in the Table. Peroxides were determined iodometrically, unless otherwise stated. A plot of the volume of oxygen absorbed against time gave a smooth curve which was a straight line between 0.5 and 1.5 mol. of  $O_2$ , and the rates were more reproducible in this region than during the initial stages when the reaction is faster and more exothermic. These linear rates are quoted in the Table.

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<sup>19</sup> P. A. McCusker, E. C. Ashby, and H. S. Makowski, *J. Amer. Chem. Soc.*, 1957, **79**, 5179.

<sup>20</sup> D. G. Hare, Thesis, London, 1960, p. 163.