Initiation Rates for Autoxidation of Trialkylboranes. Effect of a Steric Factor on the Initiation Rate

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Summary A study of the inhibition by iodine of the autoxidation of a number of trialkylboranes indicates that the rate of initiation decreases with an increase in the steric crowding about the boron atom.

TRIALKYLBORANES undergo a rapid chain autoxidation.[1] The recent discovery that iodine possesses extraordinary effectiveness as an inhibitor of such autoxidations,[2] makes possible a study of the influences of the structure of the organoborane on the rate of the initiation step.

The autoxidation proceeds through steps (1), (2), and (3).

$$R_3B + O_2 \rightarrow R_2BO_2\cdot + R\cdot \qquad (1)$$

$$R\cdot + O_2 \rightarrow RO_2\cdot \qquad (2)$$

$$RO_2\cdot + R_3B \rightarrow RO_2BR_2 + R\cdot \qquad (3)$$

The effectiveness of iodine as an inhibitor is apparently due to the fact that it can compete effectively with oxygen for the free radicals [equation (4)]. The iodine atoms evidently

$$R\cdot + I_2 \rightarrow RI + I\cdot \qquad (4)$$

cannot carry on the chain.

The competitition between oxygen and iodine for the alkyl radicals ceases at increased iodine concentrations and the reaction of alkyl radicals with oxygen is effectively prevented. Indeed, the use of high iodine concentrations (0·2M) completely stops the absorption of oxygen by solutions of organoboranes (0·5M). (It is necessary to assume that the species, $R_2BO_2\cdot$, postulated to be produced in the initiation step, is also trapped by iodine, producing $R_2BI + O_2 + I\cdot$, to account for the failure to observe any oxygen). Alkyl iodide is formed in amounts corresponding to the iodine used. Consequently, the reaction may be conveniently studied to find the effect of the structure of the organoborane on the initiation step.

Accordingly, 20 ml of a 0·5M-solution of a tributylborane in tetrahydrofuran (THF), 0·2M in iodine, was stirred vigorously in the dark at 0° under oxygen. Samples were removed periodically and analysed by g.l.c. for alkyl iodide (Table 1). In the absence of oxygen, the formation of the alkyl iodide under the same conditions and the decomposition of the alkyl iodide in oxygen is negligible. Solutions 0·5M in iodine gave similar results.

TABLE 1

Rates of initiation of autoxidation of tributylboranes

Time (h)	Butyl iodide (mmol) from R_3B		
	Bu^n_3B	Bu^i_3B	Bu^s_3B
24	0·80	0·042	0·096
48	1·5	0·090	0·20
72	2·1	0·136	0·29
Rate ($ml^{-1}min^{-1}$)	26×10^{-6}	$1·6 \times 10^{-6}$	$3·5 \times 10^{-6}$

No rate of initiation for tri-n-butylborane has been previously reported because an effective inhibitor was not available. Tri-isobutyl- and tri-s-butyl-borane are reported to have rates of initiation of 7×10^{-6} and 3×10^{-6} ml^{-1} min^{-1} at 25°, respectively, with galvinoxyl as an inhibitor.[1c] The difference in rate for tri-isobutylborane may be attributed to the fact that the inhibition rate varied greatly with the temperature for this borane.

The rates of initiation are considerably slower than the rate of autoxidation of the corresponding borane.† However, the rates of initiation, $1° > 2°$, are in the opposite order to that observed in autoxidation, namely $3° > 2° > 1°$.[3] The inhibition order is consistent with the degree of steric crowding around the boron atom. A large difference in initiation rate, which was attributed to a steric effect, has also been noticed between n-butyl- and s-butyldi-isopinocamphenylborane.[1c] To test this hypothesis, two organoboranes, one with relatively low steric crowding, *B*-n-butyl-9-borabicyclo[3,3,1]nonane (I),[4] and one with relatively high degree of steric crowding, tris-(2-butyl-3-methyl)borane (II)[5] were subjected to autoxidation with added iodine and compared to Bu^n_3B and Bu^s_3B. The results are given in Table 2.

TABLE 2

Inhibition of the autoxidation of trialkylboranes by iodine

Organoborane[a]	Iodine mol %	Inhibition period[b] min
Bu^n_3B	5·0	12·5
(I)	5·0	0·4
Bu^s_3B	0·5	12
(II)	0·5	164

[a] 10 mmol R_3B in 20 ml THF at 0°, 100% oxygen. [b] Time for iodine to disappear, followed by rapid oxygen absorption.

The sterically open borane, (I), has a very short, induction period and the sterically crowded borane, (II), a very long one. The induction period is directly related to the relative rate of initiation. Thus, increased crowding around the boron atom has a marked effect on the rate of initiation of autoxidation.

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† Under these conditions, in the absence of iodine, such solutions absorb one mol of oxygen per mol of borane in 1 min.

[1] (a) H. C. Brown, M. M. Midland, and G. W. Kabalka, *J. Amer. Chem. Soc.*, 1971, **93**, 1024; (b) A. G. Davies and B. P. Roberts. *J. Chem. Soc.* (*B*), 1967, 17; (c) P. G. Allies and P. B. Brindley, *ibid.*, 1969, 1126; (d) A. G. Davies and B. P. Roberts, *ibid.*, p. 311,

[2] M. M. Midland and H. C. Brown, *J. Amer. Chem. Soc.*, 1971, **93**, 1506; (b) J. Grotewold, J. Hernandez, and E. A. Lissi, *J. Chem. Soc.* (*B*), 1971, 182.

[3] O. Grummitt, *J. Amer. Chem. Soc.*, 1942, **64**, 1811.

[4] E. F. Knights and H. C. Brown, *J. Amer. Chem. Soc.*, 1968, **90**, 5281.

[5] H. C. Brown and G. Zweifel, *J. Amer. Chem. Soc.*, 1961, **83**, 1241.