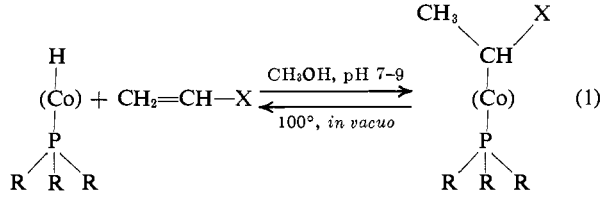
Table I. Wavelengths and Intensities of the CT Absorption of Hydridocobaloximes in Three Solvents

In-plane ligand[a]	Axial base	λ_{max}, mμ (ε)[c] *n*-Hexane	C_6H_6	CH_3OH
dmg	$P(n\text{-}C_4H_9)_3$	565 (6.0×10^3)	592 (5.8×10^3)	614 (5.0×10^3)
dmg	$P(C_2H_5)_2C_6H_5$	565 (6.2×10^3)	564 (6.0×10^3)	620 (5.2×10^3)
dmg	$P(C_6H_5)_3$	*b*	587 (4.0×10^3)	607 (4.5×10^3)
dmg	$C_6H_{11}NC$	*b*	617 (4.5×10^3)	614 (3.0×10^3)
$dmgB_2F_4$	$P(n\text{-}C_4H_9)_3$	*b*	522 (4.0×10^3)	650 (4.0×10^3)
$dmgB_2F_4$	$P(C_2H_5)_2C_6H_5$	*b*	600 (5.0×10^3)	617 (4.8×10^3)
$dmgB_2F_4$	$P(C_6H_5)_3$	617 (6.0×10^3)	587 (4.0×10^3)	607 (5.0×10^3)
$dmgB_2F_4$	Pyridine	*b*	637 (3.0×10^3)	613 (3.8×10^3)
dpg	$P(C_6H_5)_3$	*b*	637 (4.2×10^3)	640 (3.9×10^3)

[a] dmg = dimethylglyoxime; dmg B_2F_4 = dmg ligand in which the oxime protons are substituted by BF_2 groups; dpg = diphenylglyoxime. [b] Hydride insoluble or unstable in *n*-hexane. [c] Values of ε approximate.

hydridocobaloximes in nonpolar solvents, several were characterized in solution by their optical absorption spectra. All hydridocobaloximes exhibit an intense, solvent-dependent charge-transfer absorption in the visible region. Values of λ_{max} (ε) for a number of hydrides are given in Table I. The dark violet H–Co(dmg)$_2$py is formed on reducing Cl–Co(dmg)$_2$py with excess $NaBH_4$ in a pH 7 phosphate-buffered 50% aqueous methanolic suspension at 20°, but decomposes slowly at room temperature. The hydridocobaloximes with imidazole or benzimidazole as the axial ligands, however, are already too unstable to be isolated even at low reaction temperatures.

All hydridocobaloximes react with alkyl halides in protic media to produce alkylcobaloximes at rates comparable to those observed[6] with the free Co(I) nucleophiles. In carefully dried and methanol-free *n*-hexane or benzene, **1**, surprisingly, is *unreactive* with alkyl halides, ethylene oxides, ethyl acrylate, or acrylonitrile. The $3d_{z^2}$ orbital in **1** thus is effectively screened by the proton. In aqueous methanol **1** reacts with vinylogs such as acrylonitrile or acrylates to yield the α-substituted ethylcobaloxime derivatives. This reaction is characteristic of hydridocobaloximes[2] and hydridorhodoximes;[7] with the free nucleophiles the corresponding β-substituted ethylcobaloximes are formed.[2] On heating, the reverse reaction occurs, providing an example for a hydride elimination in cobaloxime chemistry (eq 1; X, *e.g.*, CN or COOR). The thermolysis at



(1)

100° *in vacuo* of α-cyanoethyl(tributylphosphine)-cobaloxime represents a convenient laboratory method for the synthesis of solvent-free **1** in essentially quantitative yield, and in analytical purity. (*Anal.* Calcd for **1**: C, 48.77; H, 8.59; N, 11.37; Co, 11.96. Found: C, 48.39; H, 8.21; N, 11.52; Co, 11.40.) The product is also identical in every respect with the solvent-free hydride obtained by the alternative method described above, and exhibits the ir Co–H stretch at 2240 cm^{-1} (Nujol mull under N_2). The reverse reaction of **1** with acrylonitrile in CH_3OH at pH 7–9 affords the known[2] α-cyanoethyl(tributylphosphine)cobaloxime in 80% isolated yield (the reaction is best conducted employing a 20-fold excess of acrylonitrile, maintaining strictly anaerobic conditions). The same compound may be obtained by generating the hydridocobaloxime *in situ*, using methods described in ref 2. The formation of **1** is also observed on heating higher alkylcobaloximes containing hydrogen in the β position and $P(n\text{-}C_4H_9)_3$ as the axial base. Hydride elimination reactions may be important in cobamide coenzyme catalyzed processes and are presently being investigated.[8]

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G. N. Schrauzer,* R. J. Holland
Department of Chemistry
The University of California at San Diego
Revelle College, La Jolla, California 92037
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(6) G. N. Schrauzer and E. Deutsch, *J. Amer. Chem. Soc.*, **91**, 3341 (1969).
(7) J. H. Weber and G. N. Schrauzer, *ibid.*, **92**, 726 (1970).

Iodine as an Exceptionally Favorable Inhibitor for the Reaction of Oxygen with Trialkylboranes. Evidence for a Very Slow Initiation Step in the Autoxidation of Organoboranes

Sir:

The very rapid reaction of trialkylboranes in tetrahydrofuran (THF) solution with oxygen[1] is strongly inhibited by the presence of small amounts of elemental iodine. Indeed, the presence of iodine in appreciable concentration, 0.2 *M*, effectively prevents the uptake of oxygen by 0.5 *M* solutions of representative organoboranes over periods as long as several days. Consequently, the reaction of oxygen with trialkylboranes must involve a relatively slow rate of radical initiation, with a very fast rate of chain propagation.

The facile autoxidation of organoboranes was long believed to be a nonradical process because many of the usual radical inhibitors, such as hydroquinone, had no apparent effect upon the reaction.[2] The oxidation of optically active 1-phenylethylboronic acid gave racemic product and this was considered to be suggestive of a process involving radicals.[3] Indeed, it was observed that the autoxidation of this boronic acid exhibits a remarkable induction period in the presence of added inhibitors, such as copper(II) *N*,*N*-dibutyldithiocarbamate and galvinoxyl.[3] It was then discovered

(1) H. C. Brown, M. M. Midland, and G. W. Kabalka, *J. Amer. Chem. Soc.*, **93**, 1024 (1971).
(2) M. H. Abraham and A. G. Davies, *J. Chem. Soc.*, 429 (1959).
(3) A. G. Davies and B. P. Roberts, *ibid.*, *B*, 17 (1967).

that galvinoxyl also effectively inhibits the autoxidation of many other boranes.[3,4] However, tri-*n*-butylborane provided a notable exception. In this case the autoxidation was not inhibited by galvinoxyl, but only slightly retarded.[4b]

We recently observed that 0.5 *M* THF solutions of trialkylboranes undergo very rapid uptake of oxygen and that such oxidations can be readily utilized to provide essentially quantitative yields of alcohols.[1] The rate of oxygen absorption is conveniently followed by use of the automatic gas generator previously developed for hydrogenation.[5] Accordingly, we explored the effect on the rate of uptake of oxygen of various added materials. To our surprise, added iodine proved to be an exceptionally effective inhibitor.[6,7] Indeed, it proved effective even for tri-*n*-butylborane, which had previously proven resistant to the operation of galvinoxyl.[4b]

For example, exposure of a 0.5 *M* solution of tri-*n*-butylborane in THF at 0° to 1 atm oxygen in the automatic generator results in a rapid uptake of 1 mol of oxygen/mol of borane in a matter of 1–2 min. The presence of 5 mol % of iodine in solution effectively halts all uptake of oxygen for 12.5 min. At that time the iodine color vanishes and the rate of oxygen absorption is approximately that observed in the absence of the inhibitor. Similar results were realized with *n*-hexane as solvent.

The presence of a methyl substituent in the 2 position, as in tris(2-methyl-1-pentyl)borane, results in a much longer inhibition period. Thus, as little as 1 mol % of iodine produces an inhibition period of 32 min. However, the inhibition of the oxidation of *sec*-alkylboranes can be even more effective. Thus, 1 mol % of iodine causes an inhibition period of 43 min in the oxidation of tri-*sec*-butylborane under these conditions. The experimental results are summarized in Table I.

The effectiveness of iodine as an inhibitor increases considerably with increasing initial concentrations of the halogen. Indeed, 0.5 *M* solutions of tri-*n*-butylborane, tri-*sec*-butylborane, and triisobutylborane in THF containing 0.2 *M* iodine failed to reveal any significant oxygen uptake over several days.

The long induction periods produced by iodine suggest that the oxidation of organoboranes must involve a relatively slow initiation stage, followed by a highly efficient chain propagation stage. Oxygen reacts with the organoborane to produce alkyl radicals (eq 1), followed by reaction of these radicals with oxygen to produce alkylperoxy radicals (eq 2), which attack the organoborane to displace alkyl radicals to carry on the chain. Iodine traps the alkyl radicals producing iodine atoms which must be incapable of propagating

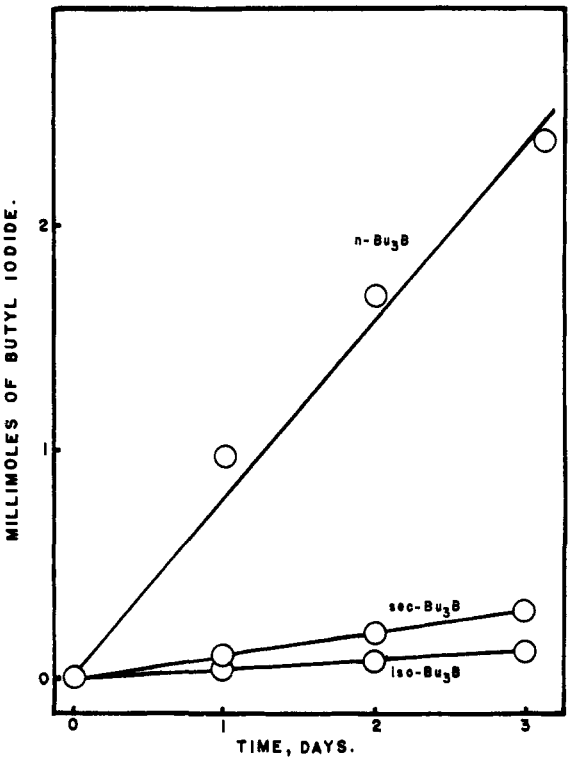

Figure 1. Iodine-inhibited oxidation of the tributylboranes in tetrahydrofuran solution at 0°.

the chain (eq 3). At low iodine concentrations there

$$R_3B + O_2 \longrightarrow R\cdot \quad (1)$$

$$R\cdot + O_2 \longrightarrow RO_2\cdot \longrightarrow \text{chain} \quad (2)$$

$$R\cdot + I_2 \longrightarrow RI + I \longrightarrow \text{no chain} \quad (3)$$

must be a competition between the reaction of the alkyl radical with oxygen, favoring the chain pathway, and the reaction of the radical with iodine. At the higher iodine concentrations, oxygen must fail to compete effectively and the reaction then follows eq 3. This accounts for the increasing molar effectiveness of iodine at the higher concentrations. It suggests that at high iodine concentrations very little of the reaction should follow the chain pathway, so it should become possible to follow the rate of initiation, the rate of production of alkyl radicals through the reaction of oxygen with the organoborane.

Table I. Inhibition of the Autoxidation of Trialkylboranes by Iodine

Organoborane[a]	Iodine, mol %	Inhibition period, min[b]
Tri-*n*-butylborane[c]	5	12.5
Tris(2-methyl-1-pentyl)-borane	1	32
Tri-*sec*-butylborane	0.5	12
	1	43
	2	150
Tricyclohexylborane	1	34
Tri-*exo*-norbornylborane	1	17

[a] All reactions were carried out in the automatic generator using 10 mmol of organoborane in 20 ml of THF at 0°. [b] Time for disappearance of the iodine color, followed by rapid uptake of oxygen. [c] Reactions run in *n*-hexane behaved similarly.

(4) (a) P. G. Allies and P. B. Brindley, *Chem. Ind. (London)*, 319 (1967); (b) P. G. Allies and P. B. Brindley, *ibid.*, 1439 (1968); (c) P. G. Allies and P. B. Brindley, *J. Chem. Soc. B*, 1126 (1969); (d) A. G. Davies and B. P. Roberts, *ibid.*, 311 (1969).

(5) C. A. Brown and H. C. Brown, *J. Amer. Chem. Soc.*, **84**, 2829 (1962). We utilized a commercial model of the hydrogenator available from Delmar Scientific Laboratories, Maywood, Ill. 60154, adapted for the generation of oxygen.[1]

(6) Iodine had been previously tested in an attempt to inhibit the autoxidation of triethylborane, but was reported to be not effective: R. L. Hansen and R. R. Hamann, *J. Phys. Chem.*, 67, 2868 (1963). We are unable to account for this difference in results.

(7) Alkyl iodides did not inhibit the rate of oxygen uptake, but caused the reaction to take a new, interesting course: A. Suzuki, S. Nazowa, M. Harada, M. Itoh, H. C. Brown, and M. M. Midland, *J. Amer. Chem. Soc.*, **93**, 1508 (1971).

Accordingly, 20 ml of 0.5 *M* solutions of tri-*n*-butylborane, tri-*sec*-butylborane, and triisobutylborane in THF, 0.2 *M* in iodine, contained individually in a 100-ml flask maintained at 0° was attached to a Brown apparatus[5] previously flushed with oxygen. The apparatus was further flushed by injecting 5 ml of 30% hydrogen peroxide into the generator. The flasks were stirred vigorously in the dark at 0° for several days. Samples were removed periodically and analyzed by glpc for butyl iodide. The results are shown graphically in Figure 1. It should be noted that the moles of butyl iodide produced are roughly equal to the number of moles of iodine which disappears in the course of the reaction. In the absence of oxygen, the formation of butyl iodides under the same conditions is negligible.

The results show that the rate of production of the iodide from tri-*n*-butylborane is considerably greater than those from triisobutylborane and tri-*sec*-butylborane. According to the arguments presented these must be equivalent to the rates of formation of free radicals from the reaction of oxygen with the organoboranes. The observed relative rates, $n\text{-Bu}_3\text{B} >> sec\text{-Bu}_3\text{B} > i\text{-Bu}_3\text{B}$, are very different from those observed for the oxidation process, in which the order for various alkyl derivatives is tertiary > secondary > primary.[8] Consequently, the chain-propagation step must be more favorable for tri-*sec*-alkylboranes than for the primary derivatives. The difference in the apparent rates of the initiation reaction is consistent with a steric interpretation. The attack of oxygen on the organoborane in the initiation state is apparently hindered by increasing crowding provided by the three alkyl groups attached to boron.

Oxygen is a diradical. The initiation stage may involve an attack on boron to displace an alkyl radical in an initial slow step[9] (eq 4). In order to account for

$$\cdot OO\cdot + R_3B \longrightarrow R_2BO_2\cdot + R\cdot \qquad (4)$$

the results, it is then necessary to postulate that iodine is effective in trapping the alkyl radical (eq 1) prior to its reaction with oxygen (eq 2), and also captures the dialkylborylperoxy radical with liberation of oxygen (eq 5) before this species can undergo other reactions incorporating oxygen into products.

$$R_2BO_2\cdot + I_2 \longrightarrow R_2BI + O_2 + I\cdot \qquad (5)$$

Iodine also effectively inhibits the rapid chain reaction involving tri-*n*-butylborane and acrolein.[10]

These results reveal that iodine is an exceptionally powerful inhibitor of the free-radical chain reactions of organoboranes. Utilization of this property of iodine has revealed that the fast reaction of oxygen with organoboranes is initiated by a slow attack of oxygen on the boron atom. Moreover, the rate of initiation is strongly dependent upon the structure of the organoborane, proceeding slower with increasing crowding about the boron atom. The free-radical reactions of the organoboranes are becoming of major theoretical and synthetic importance. The availability of an efficient inhibitor for these free-radical reactions of organoboranes provides a powerful tool for the exploration of these reactions.

(8) O. Grummitt, *J. Amer. Chem. Soc.*, 64, 1811 (1942). The rates are for the alkyl boronic acid anhydrides. We find the same order for trialkylboranes.[1]

(9) For example, a very rapid reaction of the *tert*-butoxy radical with organoboranes, *tert*-BuO· + BR_3 → *tert*-BuOBR_2 + R·, has recently been demonstrated: A. G. Davies and B. P. Roberts, *Chem. Commun.*, 699 (1969); A. G. Davies, D. Griller, B. R. Roberts, and R. Tudor, *ibid.*, 640 (1970); J. K. Kochi and P. J. Krusic, *J. Amer. Chem. Soc.*, 91, 3942 (1969).

(10) For a discussion of this interesting chain reaction with leading references see G. W. Kabalka, H. C. Brown, A. Suzuki, S. Honma, A. Arase, and M. Itoh, *ibid.*, 92, 710 (1970).

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M. Mark Midland,[11] Herbert C. Brown*
Richard B. Wetherill Laboratory, Purdue University
Lafayette, Indiana 47907
Received December 14, 1970

An Oxygen-Induced Reaction of Trialkylboranes with Alkyl Iodides. A Facile Coupling of Benzylic and Allylic Iodides *via* Triethylborane

Sir:

Trialkylboranes readily undergo an oxygen-induced reaction with organic iodides to produce the corresponding alkyl iodides. Moreover, benzylic and allylic iodides may readily be coupled in excellent yields under these mild conditions *via* the air-induced iodine abstraction using triethylborane as the reagent.

In our study of the autoxidation of trialkylboranes we observed that the addition of small amounts of iodine greatly inhibits the reaction.[1] Alkyl iodides are formed. An examination of the effect of typical organic iodides on the rate of reaction of trialkylboranes with oxygen revealed that the rate is not significantly altered (unless substantial iodine is formed), but the products are very different. Thus when 2 mmol of typical organic iodides, such as benzyl, *p*-nitrobenzyl, or allyl iodide, iodoform, or 1,2-diiodoethane, was added to 10 mmol of tri-*n*-butylborane in 20 ml of tetrahydrofuran (THF) and the resulting solution was oxidized with oxygen, *n*-butyl iodide was formed equivalent to the amount of iodide added. A small amount of bibenzyl was detected in the experiments with benzyl iodide.

The products suggest that a chain transfer occurs during the free-radical oxidation[2] (eq 1–6). The

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

$$R\cdot + R'I \longrightarrow RI + R'\cdot \qquad (2)$$

$$2R'\cdot \longrightarrow R'\text{-}R' \qquad (3)$$

$$R'\cdot + O_2 \longrightarrow R'O_2\cdot \qquad (4)$$

$$R'O_2\cdot + R_3B \longrightarrow R'O_2BR_2 + R\cdot \qquad (5)$$

$$R\cdot + O_2 \longrightarrow RO_2\cdot \qquad (6)$$

n-butyl free radicals abstract iodine from the alkyl halides even in the presence of oxygen. It appeared that by controlling the amount of oxygen introduced it would be possible to control the course of the reaction to produce alkyl iodide preferentially (eq 2). Indeed, we discovered that by introducing air at a moderate rate, 10 ml/min, through a syringe needle above the THF solution of the borane (R_3B), in the presence of an equimolar amount of allyl iodide, it was possible to produce a quantitative yield of the alkyl iodide (RI).

(1) M. M. Midland and H. C. Brown, *J. Amer. Chem. Soc.*, 93, 1506 (1971).

(2) (a) A. G. Davies and B. P. Roberts, *J. Chem. Soc. B*, 311 (1969); (b) P. G. Allies and P. B. Brindley, *ibid.*, 1126 (1969); (c) H. C. Brown, M. M. Midland, and G. W. Kabalka, *J. Amer. Chem. Soc.*, 92, 1024 (1970).