Homolytic Reactivity of Ligated Boranes toward Alkyl, Alkoxyl, and Peroxyl Radicals

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Received September 18, 1995

Introduction

Interest in organic radical reactions has increased over the last years as radical-based methods for organic synthesis have evolved.[1] In a series of papers,[2] Roberts described the investigation of the structures and elementary reactions of a variety of ligated boryl radicals $L \rightarrow B^{\cdot}H_2$ ($L = R_3N, R_3P, R_2S$) in fluid solution using EPR spectroscopy. Although ligated boryl radicals are reactive species toward various organic functional groups, the corresponding boranes are rather poor hydrogen atom donors toward alkyl radicals due to the strength of the B−H bond.[3] However, electrophilic carbon radicals (such as those formed by addition of an alkyl radical to an electron-deficient alkene) were found by Roberts[4] to react sufficiently rapidly with Bu_3PBH_2Ph to support chain reactions. For instance, this propagation step, together with halogen abstraction from RI and addition of the resulting alkyl radical to the C═C bond, is involved in the chain reaction between Bu_3PBH_2Ph, an alkyl iodide, and ethyl acrylate according to eq 1.

$$Bu_3PBH_2Ph + RI + CH_2{=}CHCOOEt \rightarrow RCH_2CH_2COOEt + Bu_3PBHIPh \quad (1)$$

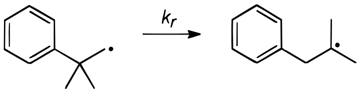
It also been shown that reactions of *t*-BuO$^{\cdot}$ with ligated boranes to generate the corresponding ligated boryl radicals is very fast,[2] although no quantitative data were given. This favorable feature permits the use of ligated boranes as donor polarity reversal catalyst for reactions in which *tert*-butoxyl radicals are not able to abstract electron-deficient hydrogen from carbon.[5]

Despite the interest in the properties of ligated boryl radicals, only a limited number of rate constants for the reactions used for their generation are reported in the literature.[2,5] Knowledge of the rate constants of radical reactions is important, for both synthetic applications and mechanistic studies, because radical-based synthetic procedures usually involve chain reactions wherein a series of propagation steps must be appropriately timed.[6]

In this paper we wish to report the results of a kinetic investigation of the generation of ligated boryl radicals by reactions with a primary alkyl radical, with *t*-BuO$^{\cdot}$, and with peroxy radicals.

Results and Discussion

Kinetic Study of the Reaction of LBH_3 with a Primary Alkyl Radical. The determination of the Arrhenius parameters for the reaction of LBH_3 with a primary alkyl radical was done by choosing as free-radical clock the neophyl rearrangement (eq 2), which has been studied in detail by Franz et al.[7] and has been already employed with success for similar purposes.[9]



(2)

The neophyl radical was formed from the corresponding bromide and the borane in benzene by a thermally initiated radical chain reaction. Relationship 3, where k_H is the rate constant for the hydrogen abstraction from the primary alkyl radical, is valid provided that the borane is the only source of hydrogen and that its concentration does not change significantly during an experiment.

$$\frac{[PhCMe_3]}{[PhCH_2CHMe_2]} = \frac{k_H}{k_r}[LBH_3] \quad (3)$$

To check the validity of eq 3, a number of experiments were carried out in which di-*tert*-butyl peroxide (0.03 M), 1-bromoadamantane (0.1 M), and the ligated borane ($L = Me_3N, Et_3N, Bu_3P$) at concentrations of 0.5−1.0 M were photolyzed at 120 °C for 3 h in a sealed glass tube using *tert*-butylbenzene free of oxygen as solvent. In the case of Bu_3PBH_3 a chain reaction ensued,[10] affording adamantane in a yield of 91% based on bromoadamantane. With Et_3NBH_3 and Me_3NBH_3 no significant amounts of reduction products were instead observed, indicating that these reagents do not support chain reactions under these conditions. Since the halogen abstraction is a fast process[11] it can be deduced that amine−boranes are very poor hydrogen atom donors toward alkyl radicals.

On this basis, we could perform the radical-clock experiments only for Bu_3PBH_3. By measuring the relative yields of *tert*-butylbenzene and isobutylbenzene at

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[1] (a) Giese, B. *Radicals in Organic Synthesis: Formation of Carbon−Carbon Bonds*; Pergamon Press: Oxford, 1986. (b) Curran, D. P. *Synthesis* **1988**, *417*, 489.

[2] (a) Dang, H. S.; Diart, V.; Roberts, B. P.; Tocher, D. A. *J. Chem. Soc., Perkin Trans. 2* **1994**, 1039. (b) Johnson, K. M.; Kirwan, J. N.; Roberts, B. P. *J. Chem. Soc., Perkin Trans. 2* **1990**, 1125. (c) Kaushal, P.; Mok, P. L. H.; Roberts, B. P. *J. Chem. Soc., Perkin Trans. 2* **1990**, 1663. (d) Kirwan, J. N.; Roberts, B. P. *J. Chem. Soc., Chem. Comm.* **1988**, 480. (e) Baban, J. A.; Roberts, B. P. *J. Chem. Soc., Perkin Trans. 2* **1987**, 497. (f) Marti, V. P. J.; Roberts, B. P. *J. Chem. Soc., Perkin Trans. 2* **1986**, 1613. (g) Baban, J. A.; Roberts, B. P. *J. Chem. Soc., Perkin Trans. 2* **1986**, 1607. (h) Green, I. G.; Roberts, B. P. *J. Chem. Soc., Perkin Trans. 2* **1986**, 1597. (i) Baban, J. A.; Goddard, J. P.; Roberts, B. P. *J. Chem. Research (S),* **1986**, 30. (j) Baban, J. A.; Marti, V. P. J.; Roberts, B. P. *J. Chem. Soc., Perkin Trans. 2* **1985**, 1723. (k) Baban, J. A.; Roberts, B. P. *J. Chem. Soc., Perkin Trans. 2* **1984**, 1717. (l) Giles J. R.; Roberts, B. P. *J. Chem. Soc., Perkin Trans. 2* **1983**, 743.

[3] Russell has demonstrated that $NaBH_4$ does not react with alkyl radicals with a measurable rate constant. Russell, G. A.; Guo, D. *Tetrahedron Lett.* **1984**, *25*, 5239.

[4] Baban, J. A.; Roberts, B. P. *J. Chem. Soc., Perkin Trans. 2* **1988**, 1195.

[5] Paul, V. P; Roberts, B. P.; Willis, C. R. *J. Chem. Soc., Perkin Trans. 2* **1989**, 1953.

[6] Newcomb, M. *Tetrahedron* **1993**, *49*, 1151 and references therein.

[7] The temperature-dependent function for neophyl rearrangment is:[8] $\log k_r$ (s^{-1}) = (11.55 ± 0.32) − (11.82 ± 0.48)/θ, where $\theta = 2.3RT$ kcal mol^{-1}.

[8] Franz, J. A.; Barrows, R. D.; Camaioni, M. *J. Am. Chem. Soc.* **1984**, *106*, 3964.

[9] For an example see: (a) Lustzyk, J.; Maillard, B.; Ingold, K. U. *J. Org. Chem.* **1986**, 5*1*, 2457. (b) Chatgilialoglu, C.; Ferreri, C.; Lucarini, M. *J. Org. Chem.* **1993**, *58*, 249.

[10] Evidence for a free-radical chain mechanism was provided by the observation that in the absence of initiator in the dark no reactions was detectable under the same conditions.

[11] Boryl radicals abstract the halogen atom rapidly from alkyl bromides. By combining data reported by Roberts,[2i] the rate constant for the bromine abstraction from ethylbromide by $(i\text{-Prop})_2EtNB^{\cdot}H_2$ at 255 K is calculated as 2×10^7 M^{-1} s^{-1}.

0022-3263/96/1961-1161$12.00/0

Table 1. Kinetic Data for the Reaction of Neophyl Radicals with Bu_3PBH_3 at Various Temperatures

T/K	$[Bu_3PBH_3]^a$/M	(k_H/k_r)/M^{-1}
313	0.61−1.35	0.336 ± 0.070
333	0.41−1.05	0.284 ± 0.058
353	0.41−1.07	0.177 ± 0.044
373	0.61−1.35	0.131 ± 0.022

[a] Range of concentration employed.

various borane concentrations, under experimental conditions in which borane is the only source of hydrogen[12] and its concentration does not change significantly during an experiment, we obtained the following Arrhenius expression in the temperature range 313−373 K:

$$\log(k_H/k_r)\ (\mathrm{M}) = (-3.09 \pm 0.70) + (3.79 \pm 1.09)/\theta \tag{4}$$

where $\theta = 2.3RT$ kcal mol^{-1} and the errors correspond to 95% confidence limit. The detailed results of the individual experiments are reported in Table 1.

The absolute values of the rate constant for hydrogen abstraction, k_H, from phosphine−borane by the primary alkyl radical can be obtained by combining eq 4 with the Arrhenius equation for the neophyl rearrangement.[7] These data are shown in Table 2 together with the analogous values for the reaction of $PhC(Me_2)CH_2^{\cdot}$ with some organometallic hydrides. The Arrhenius preexponential factors are all the same and lie in the expected range.[13] The order of reactivity is $R_3NBH_3 < R_3PBH_3 \cong Et_3SiH < (Me_3Si)_3SiH < Bu_3SnH$, and this order follows the differences in bond strength[14] which are manifest in the enthalpies of activation.

Reaction of LBH_3 with *tert*-Butoxyl Radicals. The reactivities of ligated boranes toward t-BuO$^{\cdot}$ radicals have been obtained by GC analysis by measuring the concentrations of the reagents at different times during the photochemically initiated reaction between di-*tert*-butyl peroxide and either the borane and Ph_3SiH or the borane and $(Me_3Si)_3SiH$ (eqs 5 and 6).

$$Me_3COOCMe_3 \xrightarrow{h\nu} 2Me_3CO^{\bullet}$$

$$Me_3CO^{\bullet} + LBH_3 \xrightarrow{k_5} Me_3COH + L\dot{B}H_2 \tag{5}$$

$$Me_3CO^{\bullet} + R_3SiH \xrightarrow{k_6} Me_3COH + R_3Si^{\bullet} \tag{6}$$

Table 2. Kinetic Parameters for the Reaction of Primary Alkyl Radicals with Boron, Silicon, and Tin Hydrides

hydride	log A (M^{-1} s^{-1})	E_a (kcal mol^{-1})	k_H (353 K) (M^{-1} s^{-1})	ref
Me_3NBH_3			$<1 \times 10^3$	this work
Et_3NBH_3			$<1 \times 10^3$	this work
Bu_3PBH_3	8.46	8.03	3.0×10^3	this work
Et_3SiH	8.66	7.98	5.2×10^3	9b
$(Me_3Si)_3SiH$	8.86	4.47	1.2×10^6	16
Bu_3SnH	9.07	3.69	6.1×10^6	17

Table 3. Absolute Rate Constants for the Reaction of *tert*-Butoxyl Radicals with Several Substrates at 298 K

hydride	solvent	k_H (298 K) (M^{-1} s^{-1})	ref
Me_3NBH_3	t-butylbenzene	4.1×10^7	this work
	pyridine	2.1×10^8	this work
Et_3NBH_3	t-butylbenzene	2.6×10^7	this work
	pyridine	1.3×10^8	this work
Bu_3PBH_3	benzene	2.1×10^7	this work
	pyridine	6.1×10^7	this work
Ph_3PBH_3	benzene	1.2×10^7	this work
	pyridine	6.3×10^7	this work
$PhCH_3$	benzene	2.3×10^5	19
Ph_3SiH	benzene	1.0×10^7	19
$(Me_3Si)_3SiH$	benzene	1.0×10^8	20
Bu_3SnH	benzene	2.1×10^8	19

Values of k_5/k_6 were calculated from the loss of starting material by using the method of Ingold and Shaw.[18] By using $k_6 = 1.1 \times 10^7$ for Ph_3SiH[19] and $k_6 = 1.0 \times 10^8$ for $(Me_3Si)_3SiH$[20] we obtained average values of k_5 at 298 K for the reaction of *tert*-butoxyl radicals with the studied ligated boranes (see Table 3).[21] The reported data confirm the high reactivity of ligated boranes toward *tert*-butoxy radicals predicted by Roberts[2] for the hydrogen abstraction.

This high reactivity was attributed by Roberts and coworkers[4] to polar effects causing lower than expected activation energies; actually, the alkoxy radical being highly electrophilic and the hydrogens attached to the boron atom relatively electron rich, polar structures like **1**, may contribute significantly to the transition state.

$$[t\text{-ButO}^{-}\text{H}^{\bullet}\text{H}_2\text{B}{-}\text{L}^{+}]$$

1

This hypothesis is strongly supported by the remarkable increase of the rate constant for hydrogen abstraction observed by carrying out the reaction in a solvent like pyridine,[22] characterized by a larger dielectric constant than benzene (see Table 3).

Autoxidation of Ligated Boranes. With the aim of estimating the rates of reaction of boranes with peroxyl radicals, we have also studied the autoxidation of Me_3NBH_3, Et_3NBH_3, and Bu_3PBH_3 in the presence of a radical initiator in air under controlled conditions.[23] At variance with trialkylboranes which undergo autoxidation so easily that they inflame in air,[24] ligated boranes are much more stable. In fact, an attempted autoxidation of Me_3NBH_3, Bu_3PBH_3, and Bu_3PBH_2Ph was tried previously,[4] but no oxygen consumption was noted in the conditions employed.

We have carried out the autoxidation by following the oxygen uptake with a method based on the variation of

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[12] The value obtained in this way does not distinguish between sites of interaction of borane with primary alkyl radicals.

[13] Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley-Interscience: New York, 1976.

[14] Bond dissociation energies for the metal−hydrogen bond[15] of Bu_3SnH, $(Me_3Si)_3SiH$, and Et_3SiH are 308, 331, and 376 kJ mol^{-1}, respectively. The approximate $XH_2B{-}H$ bond calculated dissociation energies[4] of H_3NBH_3 and H_3PBH_3 are 431 and 389 kJ mol^{-1}.

[15] Kanabus-Kaminska, J. M.; Hawari, J. A.; Griller, D.; Chatgilialoglu, C. *J. Am. Chem. Soc.* **1987**, *109*, 5267.

[16] Chatgilialoglu, C.; Dickhaut, J.; Giese, B. *J. Org. Chem.* **1991**, *56*, 6399.

[17] Chatgilialoglu, C.; Ingold, K. U.; Scaiano, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 7739.

[18] Ingold, C. K.; Shaw, F. R. *J. Chem. Soc.* **1927**, 2918.

[19] Chatgilialoglu, C.; Ingold, K. U.; Lustzyk, J.; Nazran, A. S.; Scaiano, J. C. *Organometallics* **1983**, *2*, 1332.

[20] Chatgilialoglu, C.; Rossini, S. *Bull. Soc. Chim. Fr.* **1988**, 298.

[21] The rate constant for hydrogen abstraction from Me_3NBH_2Thx[5] ($Thx = Me_2CHCMe_2^{-}$) and Et_2SBH_3[2b] have been previously estimated to be 4.7×10^7 at 189 K and 1×10^6 M^{-1} s^{-1} at 165 K, respectively.

[22] Although, in principle, exchange with pyridine to give a pyridine−borane could take place, the gaschromatographic analysis of the reaction mixture did not show any signal with the same retention time of an authentic sample of $PyrBH_3$.

[23] Howard, J. A. In *Free Radicals*; Kochi, J. K., Ed.; Wiley Interscience: New York, 1973; Vol. II, Chapter 12, pp 3−62.

[24] Davies, A. G. *J. Organomet. Chem.* **1980**, *200*, 87.

an EPR spectral line of a nitroxide spin probe dissolved in solution.[25] For a given borane a likely mode of reaction is that one represented by the following steps (eqs 7−10):

initiation

$$\xrightarrow{R_i} \mathrm{L\dot{B}H_2} \tag{7}$$

propagation

$$\mathrm{L\dot{B}H_2} + \mathrm{O_2} \rightarrow \mathrm{LBH_2OO^\bullet} \tag{8}$$

$$\mathrm{LBH_2OO^\bullet} + \mathrm{LBH_3} \xrightarrow{k_p} \mathrm{LBH_2OOH} + \mathrm{L\dot{B}H_2} \tag{9}$$

termination

$$2\mathrm{LBH_2OO^\bullet} \xrightarrow{k_t} \text{products} \tag{10}$$

Here, R_i is the rate at which the initiating radicals are produced and k_p and k_t represent the propagation and termination rate constants, respectively. Quantitative autoxidation studies have been performed by keeping R_i constant by thermally decomposing the azo initiator azoisobutyronitrile (AIBN).

Figure 1 reports the decrease with time of the oxygen concentration observed during the autoxidation at 50 °C of the three ligated boranes in benzene containing AIBN and 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) as spin probe.[25]

The ease of oxidation of the boranes has been estimated using a parameter independent on the concentration of the oxidizable substrate LBH_3 and of the azo initiator, that is the oxidizability, $k_p/(2k_t)^{1/2}$ (eq 11),[23] whose values for the various ligated boranes are reported in Table 4.[26]

$$\frac{k_p}{\sqrt{2k_t}} = \frac{-\mathrm{d}[\mathrm{O_2}]/\mathrm{d}t - R_i}{[\mathrm{LBH_3}]\sqrt{R_i}} \tag{11}$$

In principle, oxidizability values can not be related to changes in the nature of the substrate, since the ratio $k_p/(2k_t)^{1/2}$ can be influenced by the reactivity of the substrate, the reactivity of the peroxy radical, and the absolute magnitude of the termination rate constant. Nevertheless, in the present case it seems reasonable to assume that the different boron peroxy radicals exhibit similar reactivity in the propagation and termination reaction so that differences in the overall rate of oxidation are mainly due to differences in the reactivity of the substrate, i.e., in the B−H bond strength. Indeed, the greater reactivity is found experimentally with Bu_3PBH_3, that is with the borane characterized by the lower bond dissociation energy.[14]

It is also worth pointing out that the oxidizability is almost the same in the two amine−boranes examined, confirming that the site of attack of the peroxy radical to the ligated borane is the B−H bond. If the hydrogen abstraction would have occurred at a C−H bond of the alkyl substituents a different behavior would have been expected for the two amine−boranes.

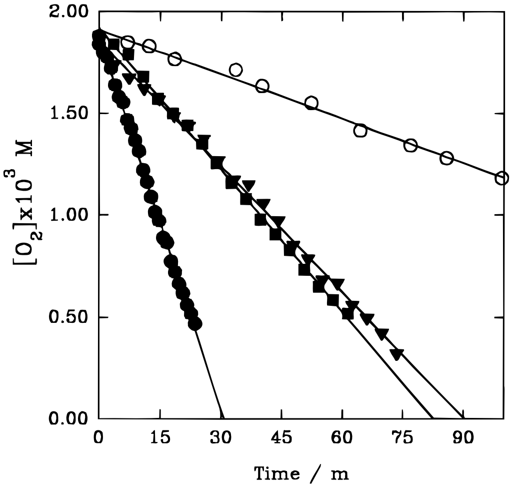

Figure 1. Time dependence of $[O_2]$ during the AIBN (27.5 mM)-initiated autoxidation of (●) Bu_3PBH_3 (1 M), (▼) Et_3NBH_3 (1 M), and (■) Me_3NBH_3 (1 M) at 50 °C in benzene containing TEMPO (5×10^{-5} M). (○) Dependence of oxygen concentration on time measured during the decomposition of AIBN (27.5 mM) in air-saturated benzene at 50 °C in the presence of α-tocopherol (5×10^{-3} M) and TEMPO (5×10^{-5} M). $R_i = 1.13 \times 10^{-7}$ M/s.

Table 4. Oxidizability $[k_p/(2k_t)^{1/2}]$ Values for Ligated Boranes Measured at 50 °C in Benzene

substrate	oxidizability/$M^{-1/2}\ s^{-1/2}$
Me_3NBH_3	8.10×10^{-4}
Et_3NBH_3	7.01×10^{-4}
Bu_3PBH_3	2.56×10^{-3}

Conclusions

Ligated boranes containing amine or phosphine ligands give rise to a hydrogen transfer reaction slow with alkyl radicals but very fast with alkoxy radicals. The rate of reaction with alkyl radicals is larger for the phosphine−borane than for the amine−boranes and, thus, is essentially determined by the strength of the B−H bond. Accordingly, Bu_3PBH_3 is able to reduce bromoalkanes in a thermally or photochemically initiated radical chain reaction, while under similar conditions, amine−boranes do not afford reduction products.

On the other hand, hydrogen transfer from the ligated boranes to *tert*-butoxyl radicals, in addition to being very fast, is scarcely affected by the nature of the ligand. An explanation of this behavior previously proposed in terms of polar effects[14] is strongly supported by the kinetic data obtained in benzene and pyridine.

In the reaction of the boranes with peroxyl radicals the actual rate constants could not be determined; however, the oxidizability values indicate a behavior intermediate between those for the reactions with alkyl and with alkoxy radicals. This suggests that polar effects are less important than in the reaction with alkoxyl radicals.

Experimental Section

Materials. Neophyl bromide[27] and di-*tert*-butyl hyponitrite[28] were prepared following the literature procedures. All other materials were commercially available.

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[25] (a) Cipollone, M.; Di Palma, C.; Pedulli, G. F. *Appl. Magn. Reson.* **1992**, *3*, 99. (b) Pedulli G. F. In *Free Radicals and Antioxidants in Nutrition*; Corongiu, F., Banni, S., Dessi, M. A., Rice-Evans, C., Eds.; Richelieu Press: London, 1993; pp 211. (c) Pedulli, G. F.; Lucarini, M.; Pedrielli, P.; Sagrini, M.; Cipollone, M. *Res. Chem. Intermed.* **1996**, *22*, 1−14.

[26] The rates of initiation, R_i, were measured by following the oxygen consumption during the thermal decomposition of AIBN, in the presence of α-tocopherol. Under these conditions oxygen is removed from the solution at the constant rate R_i by the alkyl radicals generated from the azo initiator, and the resulting peroxyl radicals, in turn, are trapped by α-tocopherol.

[27] Fainberg, A. H; Winstein, J. *J. Am. Chem. Soc.* **1956**, *78*, 2763.

[28] Mendenhall, G. D. *Tetrahedron Lett.* **1983**, *24*, 451.

General Procedure for Kinetic Measurements of the Reaction of Primary Alkyl Radicals with Ligated Boranes. A solution of neophyl bromide, Bu_3PBH_3 (in a ratio of ca. 1:20), a radical initiator, and an internal GC standard, in benzene, was degassed and sealed under argon in Pyrex ampules. The reaction mixture was thermolyzed in the temperature range 313−373 K. *tert*-Butyl hyponitrite or dibenzoyl peroxide was used as the radical initiator depending on the reaction temperature. The products of the reactions were analyzed by GC using a 30 m × 0.53 mm HP-5 column with temperature programming from 50 to 250 °C using a HP Series II chromatograph. The products of interest were identified by comparison of their retention times with authentic materials.

General Procedure for Kinetic Measurements of the Reaction of Butoxyl Radicals with Ligated Boranes. A solution of di-*tert*-butyl peroxide (0.2−0.4 M), the ligated borane (ca. 1×10^{-2} M), the silane, and an internal GC standard, in benzene or pyridine, was degassed and sealed under argon in quartz ampoules. The reaction mixture was photolyzed at room temperature for 15−30 min, and the disappearance of the products was analyzed by GC.

Autoxidation of Ligated Boranes. A solution of the borane (0.5−1.0 M), 2,2′-azobis(2-methylpropionitrile) (0.0275 M), and 2,2,6,6-tetramethylpiperidine-1-oxyl (5×10^{-5} M) in benzene was air saturated at room temperature and introduced (ca. 200 μL) into a capillary tube with the internal diameter of ca. 1.85 mm. A second capillary tube (external diameter of 1.60 mm) sealed at one end was introduced into the sample tube so to leave very little dead volume space. The oxygen uptake was followed by an EPR method previously described.[25]

Acknowledgment. Financial support from MURST and CNR is gratefully acknowledged. We also thank Mrs. C. Vignoli for assistance in preparing some samples.

JO951707K