JOC *Article*

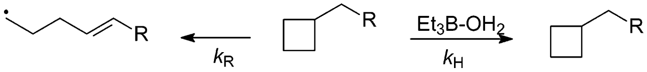
Rate Constants for Reactions of Alkyl Radicals with Water and Methanol Complexes of Triethylborane

Jing Jin and Martin Newcomb*

*Department of Chemistry, University of Illinois at Chicago, 845 West Taylor Street,
Chicago, Illinois 60607*

men@uic.edu

Received February 18, 2007



Reactions of secondary alkyl radicals with triethylborane and several of its complexes were studied. The H-atom transfer reactions from Et_3B-OH_2 and Et_3B-OD_2 were suppressed by addition of pyridine to the reaction mixture. Rate constants for reactions of secondary alkyl radicals with triethylborane and its complexes with water, deuterium oxide, methanol, and THF at ambient temperature were determined by radical clock methods. Cyclization of the 1-undecyl-5-hexenyl radical and ring opening of the 1-cyclobutyldodecyl radical were evaluated as clock reactions. The cyclobutylcarbinyl radical ring opening had the appropriate velocity for relatively precise determinations of the ratios of rate constants for H-atom transfer trapping and rearrangement, and these ratios combined with an estimated rate constant for the cyclobutylcarbinyl radical ring opening gave absolute values for the rate constants for the H-atom transfer reactions. For example, the triethylborane−water complex reacts with a secondary alkyl radical in benzene at 20 °C with a rate constant of 2×10^4 M^{-1} s^{-1}. Variable temperature studies with the Et_3B-CH_3OH complex in toluene indicate that the hydrogen atom transfer reaction has unusually high entropic demand, which results in substantially more efficient hydrogen atom transfer trapping reactions in competition with radical ring opening and cyclization reactions at reduced temperatures.

Introduction

Radical chain reactions have become an integral part of organic synthetic methodology.[1−3] The most common final step in a chain reaction sequence is radical reduction by hydrogen atom transfer, and trialkyltin hydrides often have been used as hydrogen atom donors. Tin hydrides are relatively inexpensive, they react fast enough to permit their use in low concentrations,[4] and the tin-centered radicals formed as intermediates propagate chain sequences efficiently with many radical precursors.[5] Despite these advantages, tin hydride reagents increasingly are being avoided because tin compounds are toxic and tin-containing byproducts are difficult to remove from product mixtures. To address concerns about the use of tin hydride reagents, alternative radical reducing, or hydrogen atom transfer trapping, agents have been developed in recent years.

Many useful applications of borane reagents in radical-based synthetic methodology exist,[6] and one of the more remarkable recent discoveries was that simple hydroxylic compounds (water and methanol) complexed with borane reagents can react with alkyl radicals by H-atom donation. The α-hydrogens of trialkylboranes were known to be relatively reactive toward radicals, with an estimated α-C−H bond dissociation energy (BDE) of Et_3B of only 80 kcal/mol,[7,8] and complexation of boranes with amines was known to activate B−H bonds toward reactions with radicals.[9] The recent findings demonstrated that hydroxylic hydrogen atoms in the borane complexes also are reactive. Thus, Wood and co-workers reported that the water complexes with both Et_3B and Me_3B reacted with alkyl radicals by H-atom

---

(1) Giese, B. *Radicals in Organic Synthesis: Formation of Carbon-Carbon Bonds*; Pergamon: Oxford, 1986.

(2) Jasperse, C. P.; Curran, D. P.; Fevig, T. L. *Chem. Rev.* **1991**, *91*, 1237−1286.

(3) *Radicals in Organic Synthesis*; Renaud, P., Sibi, M. P., Eds.; Wiley-VCH: Weinheim, Germany, 2001.

(4) Chatgilialoglu, C.; Newcomb, M. *Adv. Organomet. Chem.* **1999**, *44*, 67−112.

(5) Carlsson, D. J.; Ingold, K. U. *J. Am. Chem. Soc.* **1968**, *90*, 7047−7055.

(6) Darmency, V.; Renaud, P. *Top. Curr. Chem.* **2006**, *263*, 71−106.

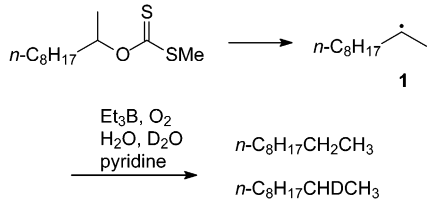
(7) Grotewold, J.; Lissi, E. A.; Scaiano, J. C. *J. Organomet. Chem.* **1969**, *19*, 431−434.

(8) Walton, J. C.; McCarroll, A. J.; Chen, Q.; Carboni, B.; Nziengui, R. *J. Am. Chem. Soc.* **2000**, *122*, 5455−5463.

(9) Paul, V.; Roberts, B. P.; Willis, C. R. *J. Chem. Soc., Perkin Trans. 2* **1989**, 1953−1961.

10.1021/jo070336s CCC: $37.00

SCHEME 1



transfer of the hydroxylic hydrogen atoms,[10] and Renaud and co-workers found that methanol similarly reacted with radicals in the presence of catechol boranes.[11] The requisite feature of these complexes is that Lewis acid−base interactions between the boranes and hydroxylic compounds substantially reduce the O−H homolytic BDEs in the complexes. Indeed, for the case of water complexed with Me_3B, the O−H BDE was computed to be reduced by 30 kcal/mol from that of the O−H bond in uncomplexed water.[10]

The use of borane-complexed alcohols and water as radical reducing agents is quite attractive due to the ease of removing boron-containing byproducts. The full potential of these reagents in radical chain reactions should become apparent as more examples of their applications are reported and with increased understanding of the mechanisms and rate constants for their reactions. In the present work, we address the reactivity and kinetics question in a radical clock[12,13] study that provided rate constants for reactions of an alkyl radical with triethylborane and its complexes of water and methanol. The rate constants at room temperature are approximately 2 orders of magnitude smaller than that of the archetypal tin hydride reagent Bu_3SnH, and hydrogen atom abstraction from the α-position of the boranes competes with abstraction of the hydroxylic H-atoms of the complexes. At reduced reaction temperatures, H-atom transfer from the Et_3B-CH_3OH complex was unexpectedly efficient in comparison to radical rearrangements, reflecting unusually high entropy demand in the transition state for the H-atom transfer reaction of the borane complex.

Results and Discussion

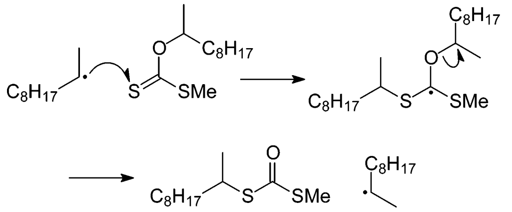
In a study patterned after that reported by Wood and co-workers,[10] the 1-methylnonyl radical (**1**) produced in chain reactions from the xanthate ester of 2-decanol was allowed to react in benzene in the presence of triethylborane with various additives present (Scheme 1). The objective was to evaluate whether the trialkylborane reagent was responsible for a portion of the H-atom transfer reactions. The yield of decane was determined by quantitative GC analysis, and, where appropriate, the percent incorporation of deuterium was determined by GC−mass spectrometry.

TABLE 1. Product Yields from Reactions of the 1-Methylnonyl Radical^{a}

equiv of Et_3B^{b}	additives (equiv)^{b}	% yield^{c}	% D^{d}
5	none	83	
5	H_2O (5)	73	
10	D_2O (5)	82	53
5	D_2O (5)	71	80
5	D_2O (5), pyridine (1)	*e*	74
5	D_2O (5), pyridine (3)	61	62
5	D_2O (5), pyridine (5)	50	33
5	D_2O (5), pyridine (10)	24	1

^{a} Reactions in benzene at room temperature with O_2 initiation. ^{b} Equivalents of borane or additive relative to the radical precursor. ^{c} Percent yield of decane. ^{d} Percentage of decane-d_1. ^{e} Not determined.

SCHEME 2



The results are in Table 1. Decane was formed in 70−80% yield with Et_3B alone or with a 1:1 mixture of Et_3B and water. For a 1:1 mixture of Et_3B with D_2O, the yield of decane was unchanged, and the amount of deuterium incorporation in the decane was ca. 80%. With D_2O present, addition of pyridine as a competitive Lewis base for Et_3B resulted in a reduction in both the yield of decane and the percentage of deuterium incorporated into the decane. Eventually, the deuterium incorporation approached zero at high pyridine concentration. Interestingly, the absolute yield of non-deuterated decane was relatively constant in the studies with D_2O and pyridine present; this suggests that a background reaction involving Et_3B reacting as a H-atom donor persisted under all conditions.

The yield of decane in the studies in Table 1 was ca. 80% under the best conditions and decreased to about 20% when a large excess of pyridine was present. The absence of deuterium in the decane in the presence of excess pyridine indicates that ca. 20% of the alkyl radicals reacted in disproportionation reactions and/or with the α-positions of (complexed) Et_3B, and these background reactions appeared to be relatively constant in all studies. Several reaction channels are available to the 1-methylnonyl radicals to account for reduced yields when efficient H-atom trapping agents are not present. Radical−radical reactions (couplings and disproportionation reactions) are possible as is alkyl radical reaction with oxygen that is admitted slowly into the reaction mixture to initiate chain reactions. Alkyl radicals also are expected to add to borane-complexed pyridine in reactions similar to those of alkyl radicals with protonated pyridines.[14,15] In addition, the alkyl radical can add to xanthate precursor at the thione sulfur to give the self-trapped product *S*-methyl-*S′*-(1-methylnonyl)dithiocarbonate (Scheme 2). The self-trapping reaction of xanthate esters is a well-known and important process in their radical chemistry,[16] and it limits yields in all reactions using xanthate esters as radical precursors.

The reaction in Scheme 2 was confirmed qualitatively by NMR spectral analysis of the crude product mixtures from reactions conducted in the presence of excess pyridine. In the NMR spectrum of the starting xanthate ester, the methine proton at C2 of the decyl group (adjacent to the oxygen atom) absorbed as a multiplet at δ 5.66−5.72. In the NMR spectra of the crude

---

(10) Spiegel, D. A.; Wiberg, K. B.; Schacherer, L. N.; Medeiros, M. R.; Wood, J. L. *J. Am. Chem. Soc.* **2005**, *127*, 12513−12515.

(11) Pozzi, D.; Scanlan, E. M.; Renaud, P. *J. Am. Chem. Soc.* **2005**, *127*, 14204−14205.

(12) Griller, D.; Ingold, K. U. *Acc. Chem. Res.* **1980**, *13*, 317−323.

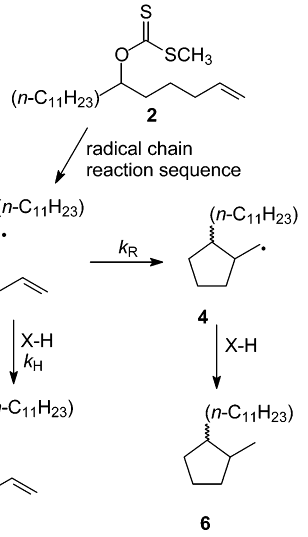
(13) Newcomb, M. *Tetrahedron* **1993**, *49*, 1151−1176.

(14) Minisci, F.; Vismara, E.; Fontana, F.; Morini, G.; Serravalle, M.; Giordano, C. *J. Org. Chem.* **1986**, *51*, 4411−4417.

(15) Minisci, F.; Vismara, E.; Fontana, F. *Heterocycles* **1989**, *28*, 489−519.

(16) Quiclet-Sire, B.; Zard, S. Z. *Top. Curr. Chem.* **2006**, *264*, 201−236.

SCHEME 3



product mixtures, this signal was lost, and a new multiplet at δ 5.02−5.08 was observed. We assume that the new signal is from the methine proton at C2 in the decyl group, now adjacent to the sulfur atom in the dithiocarbonate product.

For kinetic determinations, a chain reaction using the well-established 5-*exo* cyclization of a 5-hexenyl radical as a clock[12,13] was designed (Scheme 3). The xanthate ester **2** was employed as the precursor because xanthate esters from secondary alcohols are relatively efficient in radical generation.[16] Details for the synthesis of **2** are in the Supporting Information. The chain reaction sequence gave radical **3** that either cyclized to give a mixture of radicals **4** or reacted with a H-atom transfer agent X−H to give 1-heptadecene (**5**). Cyclic radicals **4** also can react with the H-atom trapping agent to give *cis*- and *trans*-1-methyl-2-undecylcyclopentane (**6**). The ratio of *cis*-**6** to *trans*-**6** was ca. 1:3, similar to the ratio of isomers formed in the cyclization of the 1-methyl-5-hexenyl radical.[17,18]

The kinetically important reactions in the radical clock study are the cyclization and the H-atom trapping reactions of radical **3**. The kinetics are described by eq 1, where [**5**] and [**6**] are the molar yields of the respective products, k_H is the second-order rate constant for H-atom transfer, k_R is the first-order rate constant for rearrangement (cyclization in this case), and [X−H] is the concentration of trapping agent.[13] A plot of acyclic product **5** to cyclic product **6** as a function of concentration of trapping agent X−H will have a slope of k_H/k_R.

$$[\mathbf{5}]/[\mathbf{6}] = (k_H/k_R)\,[\mathrm{X{-}H}] \tag{1}$$

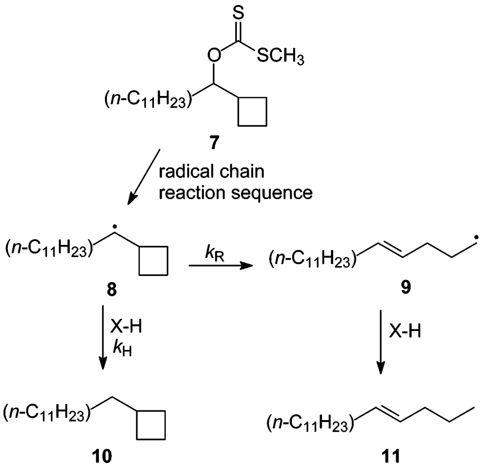
A series of reactions was conducted with precursor **2** and varying concentrations of 1:1 mixtures of Et_3B with water, deuterium oxide, and methanol, and the product ratios were determined by GC. The ratios of rate constants (k_H/k_R) from these studies are listed in Table 2. Due to the relatively small rate constant for the trapping reaction, radical **3** mainly cyclized, giving cyclic to acyclic product ratios in the range of 15:1 to 50:1, and the error in the ratio of products determined from the slopes of the plots according to eq 1 approached 20% of the absolute value. Nonetheless, the values of k_H determined in these studies appear to be internally consistent with those obtained with a second radical clock (see below).

TABLE 2. Rate Constants for Reactions of Radical Trapping Agents with Secondary Alkyl Radicals at Room Temperature[a]

radical	complex	k_H/k_R (M^{-1})[b]	k_H ($M^{-1}\,s^{-1}$)
3	Et_3B-H_2O	0.12 ± 0.02	2×10^4
	Et_3B-D_2O	0.04 ± 0.005	0.8×10^4
	Et_3B-CH_3OH	0.11 ± 0.02	2×10^4
8	Et_3B	4.2 ± 0.3	0.4×10^4
	Et_3B-H_2O	20.0 ± 1.0	2.0×10^4
	Et_3B-D_2O	8.2 ± 0.8	0.8×10^4
	Et_3B-CH_3OH	11.2 ± 1.4	1.1×10^4
	Et_3B-THF	5.2 ± 0.2	0.5×10^4

[a] For calculations of k_H, the rate constant for cyclization of radical **3** was assumed to be $2 \times 10^5\ s^{-1}$, and the rate constant for ring opening of the cyclobutylcarbinyl radical **8** was assumed to be $1 \times 10^3\ s^{-1}$. [b] The stated errors in the relative rate constants are at one standard deviation for the least-squares fits of the data.

SCHEME 4



A slower radical clock reaction was desired so that comparable amounts of unrearranged and rearranged products would be formed in reactions with the borane complexes. With such a clock, the precision in the product ratios would be expected to improve considerably. Ring openings of cyclobutylcarbinyl radicals are known to have rate constants at ambient temperature that are approximately 2 orders of magnitude smaller than the rate constants for cyclizations of 5-hexenyl radicals.[13,19,20] Thus, the cyclobutylcarbinyl radical **8** from precursor **7** was envisioned as a useful clock (Scheme 4). As in the previous study with **3**, radical **8** can be trapped by X−H with rate constant k_H to give the cyclobutane product **10** or can rearrange with rate constant k_R, and the acyclic radical(s) can then react with the H-atom donor. In practice, we observed that *trans*-4-hexadecene (**11**) was the only significant isomer formed in the radical ring opening. The ratio of products **10**/**11** can be used to determine the ratio of rate constants according to eq 2.

$$[\mathbf{10}]/[\mathbf{11}] = (k_H/k_R)\,[\mathrm{X{-}H}] \tag{2}$$

The synthesis of precursor **7** is described in the Supporting Information. Xanthate **7** was allowed to react with H-atom

---

[17] Walling, C.; Cioffari, A. *J. Am. Chem. Soc.* **1972**, *94*, 6059−6064.

[18] Beckwith, A. L. J.; Easton, C. J.; Lawrence, T.; Serelis, A. K. *Aust. J. Chem.* **1983**, *36*, 545−556.

[19] Beckwith, A. L. J.; Moad, G. *J. Chem. Soc., Perkin Trans. 2* **1980**, 1083−1092.

[20] Ingold, K. U.; Maillard, B.; Walton, J. C. *J. Chem. Soc., Perkin Trans. 2* **1981**, 970−974.

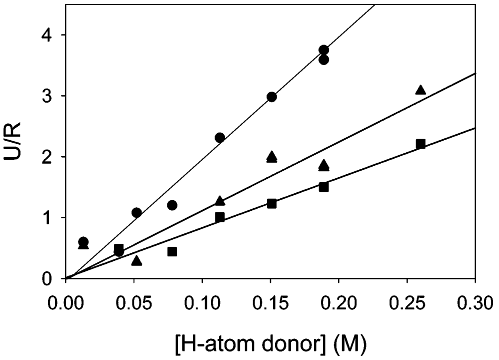


FIGURE 1. Product ratios from reactions of radical **8** in the presence of Et_3B with water (●), with deuterium oxide (■), or with methanol (▲). U/R is the ratio of the cyclobutyl product **10** to ring opened product **11**. The lines are least-squares fits for each data set.

trapping agents at varying concentrations, and the products were determined by GC analysis. Hydrocarbon products **10** and **11** were identified by comparison to authentic samples. The yields of hydrocarbons **10** and **11** were high (>70%) with Et_3B-H_2O, consistent with expectations that the generation of **8** from a radical chain reaction of **7** would be relatively efficient. Also as expected, the ratios of unrearranged to rearranged products were considerably larger than those from reactions of radical **3**.

Figure 1 shows representative results for the reactions of radical **8** in the presence of Et_3B with additives. The ratio of **10** to **11** is plotted against the concentration of the Et_3B complex, and the slope of these plots is the ratio of rate constants k_H/k_R. The near-zero intercepts of these plots are noteworthy because they show that the radical reaction is not reversible (see below). Complete results for the studies with radical **8** are given in the Supporting Information, and the ratios of rate constants obtained in these studies are listed in Table 2. In most of the experiments, the relative amount of unrearranged product was in the range of 20−80%, and good precision was obtained in the relative rate constants.

When a radical clock study is performed with a relatively slow trapping agent, one should determine whether the clock reaction is reversible under the reaction conditions. That can be established in the type of study performed here because the intercepts of the plots of product ratios versus concentration of trapping agent would be non-zero if the radical reaction was reversible.[13] As indicated in Figure 1 and listed in the Supporting Information, we found zero intercepts within experimental error for all reactions with radical **8**, thus ensuring that the reactions were not reversible.

The ratios of rate constants determined experimentally can be used to calculate absolute rate constants k_H if the rate constant for the rearrangement reaction is known. This "radical clock" method is commonly employed with the assumption that the rate constants for the rearrangement reactions are not affected by any special reaction conditions. The rate constants for simple radical cyclization and ring opening reactions such as those used here are generally not subject to noticeable solvent effects.[13] Nonetheless, it is possible, in principle, that Lewis acids will affect the kinetics of radical reactions, and Horn and Clark explored computationally the possibility that Lewis acid complexation will accelerate a 5-*exo* radical cyclization such as that in radical **3**.[21] The computational results suggest that an alkali metal ion will accelerate the radical cyclization in the gas phase, but little evidence for such an acceleration in condensed phase is available, probably because the binding constants for formation of complexes between an alkene and an alkali metal ion are small. For the ring opening reaction of radical **8**, Lewis acids should not affect the reaction because a complex will not be present in condensed phase.

With the caveat that the rate constant for cyclization of radical **3** might be affected by the Lewis acid Et_3B, we used estimated rate constants for cyclization of **3** and ring opening of **8** to calculate second-order rate constants for the H-atom transfer reactions. Both the 5-hexenyl radical and the 1-methyl-5-hexenyl radical cyclize at 20 °C with rate constants of $k_R = 2 \times 10^5$ s^{-1},[17,18,22,23] and we assumed that this would be equal to the rate constant for cyclization of **3**. For the ring opening of radical **8**, we assumed that the rate constant would be equal to that for ring opening of the cyclobutylcarbinyl radical at 20 °C, $k_R = 1000$ s^{-1}.[4,19,24] These values for k_R and the experimental ratios of rate constants gave the values for k_H that are listed in Table 2.

The values of the absolute rate constants k_H might have systematic errors due to the assumed rate constants for the rearrangements, but those errors are not likely to be as large as a factor of 2. More importantly, the relative rate constants for two trapping agents reacting with the same radical clock will have good accuracy. Thus, triethylborane complexed with water reacted with radical **8** five times as fast as the uncomplexed borane reagent, and the presence of the Lewis basic solvent THF as an additive had little effect on the reactivity of the α-hydrogens of Et_3B. Assuming that the α-hydrogen atoms in Et_3B complexed with H_2O and D_2O have the same reactivity as in the uncomplexed borane, one can factor out an equal contribution to the kinetics of reactions of the borane α-hydrogens from the H_2O and D_2O reactions to give a kinetic isotope effect for reaction of the water complexes with radical **8** of $k_H/k_D = (2.0 - 0.4)/(0.8 - 0.4) = 4$.

The rate constants we determined are for reactions at room temperature, but one can make qualitative predictions about the rate constants at other temperatures because various second-order hydrogen atom transfer reactions have relatively consistent entropy demands. More importantly for synthetic considerations, one can predict that the hydrogen atom transfer reactions from the triethylborane−water and −methanol complexes should become increasingly competitive with radical rearrangements such as we used for the radical clocks in this work. For example, the log *A* values for many hydrogen atom transfer reactions to carbon-centered radicals are in the range of 8−9.[4,13] The 5-*exo* radical cyclization reactions, such as the cyclization of radical clock **3**, have entropy of activation terms that are less negative than those for second-order bimolecular H-atom transfer reactions; one can use an approximate value of log $A = 10$ for such

---

[21] Horn, A. H. C.; Clark, T. *J. Am. Chem. Soc.* **2003**, *125*, 2809−2816.

[22] Chatgilialoglu, C.; Ingold, K. U.; Scaiano, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 7739−7742.

[23] Lusztyk, J.; Maillard, B.; Deycard, S.; Lindsay, D. A.; Ingold, K. U. *J. Org. Chem.* **1987**, *52*, 3509−3514.

[24] In the original study of ring openings of cyclobutylcarbinyl radical ring openings, the value obtained for the rate constant for cyclobutylcarbinyl ring opening was $k = 500$ s^{-1} at ambient temperature, but the value assumed for the rate constant for the competing reaction, Bu_3SnH trapping of an alkyl radical, was 1×10^6 M^{-1} s^{-1} (ref 19). The currently accepted value for the rate constant for the Bu_3SnH reaction is 2×10^6 M^{-1} s^{-1} (ref 4).

[25] For a reaction with $\Delta S^{\ddagger} = 0$ eu at room temperature, the equivalent Arrhenius function term is log $A = 13.1$.

[26] Wilt, J. W.; Lusztyk, J.; Peeran, M.; Ingold, K. U. *J. Am. Chem. Soc.* **1988**, *110*, 281−287.

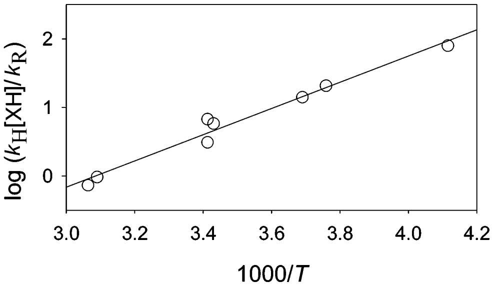


FIGURE 2. Logarithm of ratio of products **10** to **11** as a function of temperature for reactions in toluene in the presence of 0.26 M Et_3B-CH_3OH. Note that log([**10**]/[**11**]) = log(k_H/k_R).

a cyclization.[13] Radical ring opening reactions, such as ring opening of radical clock **8**, have even less negative or slightly positive entropies of activation,[13] and one can estimate the log A term for ring opening of **8** as log $A \approx 13$.[25] The result is that one would predict that the hydrogen atom transfer reaction from Et_3B-OH_2 or Et_3B-CH_3OH will become increasingly competitive with a 5-*exo* radical cyclization or a radical ring opening as the reaction temperature is decreased.

The above prediction was tested in the following study. Radical clock **8** was allowed to react in a series of reactions at various temperatures and with an equal concentration of Et_3B-CH_3OH (0.26 M) in each reaction. The relative ratio of unrearranged to rearranged product ([**10**]/[**11**]) was 0.7 at 53 °C but increased at lower temperatures to give, ultimately, a ratio of 80 at −30 °C. These results are qualitatively in line with the predicted temperature-dependent behavior.

A quantitative evaluation of the variable temperature results indicates that the hydrogen atom transfer reaction from Et_3B-CH_3OH is more entropically demanding than initially assumed. The product ratios versus temperature are presented in Figure 2 in the form of a relative Arrhenius plot. For these data, the relative Arrhenius function in eq 3 would apply, where the subscripts H and R represent the hydrogen atom transfer reaction and ring opening reaction of **8**, respectively. The plot in Figure 2 gives $\Delta\log A = (-6 \pm 1)$ and $\Delta E_a = (-8.8 \pm 1.2)$ kcal/mol, where the errors are at 2σ.

$$\log(k_H/k_R) = (\log A_H - \log A_R) - (E_{aH} - E_{aR})/2.3RT \qquad (3)$$

Another qualitative evaluation of the temperature dependence of hydrogen atom transfer from triethylborane complexes was made using the 5-*exo* cyclization of radical **3**. The entropic demand of a 5-*exo* radical cyclization is more negative than that for ring opening of a cyclobutylcarbinyl radical but not as negative as that of the bimolecular hydrogen atom transfer reaction. Thus, a reduction of reaction temperature was expected to result in more efficient trapping of the acyclic radical **3**. At 20 °C with 0.1 M Et_3B-CH_3OH, acyclic product **5** was only 2% of the product mixture. By increasing the concentration of Et_3B-CH_3OH to 0.3 M and reducing the reaction temperature to −30 °C, the relative yield of acyclic product **5** was increased to 20%.

For perspective, it is useful to compare the reactivity of the Et_3B-OH_2 complex as a H-atom donor for alkyl radicals with the reactivities of other H-atom transfer trapping agents. Group 14 metal hydrides are commonly used in synthesis, and rate constants for archetypal members of this group reacting with alkyl radicals are listed in Table 3.[4,22,26−31] Some Group 16 H-atom donors also are listed in Table 3. Note that the reactivity of group 14 metal hydrides is mainly a function of the difference in bond dissociation energy (BDE) for the donor[4,32−34] and a C−H bond of an alkyl group; the BDE values for primary and secondary C−H bonds are 101.1 and 98.6 kcal/mol, respectively.[35,36] In the case of group 16 donors, high reactivity results from both differences in BDEs[29,35,37−39] and favorable polar effects for reactions of electron-rich carbon radicals with an electron-deficient hydrogen atom of the donor.

TABLE 3. Rate Constants for Reactions of H-Atom Donors with Alkyl Radicals at Room Temperature and Bond Dissociation Energies[a]

donor	k_H (M^{-1} s^{-1})	ref	BDE (kcal/mol)[b]	ref
Et_3SiH[c]	3.2×10^2	4	90	32
Et_3B[d]	4×10^3	this work	80	7
Et_3B-H_2O	2.0×10^4	this work	86[e]	10
Bu_3GeH	1.0×10^5	26	83	33
$((CH_3)_3Si)_3SiH$	3.9×10^5	27	79	32
Bu_3SnH	2.2×10^6	4, 22	74	34
t-BuSH	6×10^6	28	89	38
PhSH	9×10^7	29, 30	83	29, 35
PhSeH	1.2×10^9	30, 31	78	39

[a] Rate constants for reactions with primary and/or secondary alkyl radicals. [b] BDE = homolytic bond dissociation energy. The BDE values listed are from original literature, but re-evaluation of the data for group 14 hydrides indicates that the scale should be shifted upward (see ref 4). [c] Rate constant for reaction of the Si−H bond only; the α-hydrogens of the ethyl groups also react. [d] Rate constant for reaction of Et_3B is assumed to involve only the α-hydrogen atoms. [e] Computed BDE for the O−H bond in the Me_3B-H_2O complex.

Relatively unreactive H-atom donors, such as Et_3SiH, are not useful in synthesis because they react too slowly with carbon radicals, and radical−radical coupling reactions dominate when chain reactions are attempted. The germanium hydride Bu_3GeH reacts fast enough to be used in synthesis,[26] and the Et_3B-H_2O complex has similar reactivity. Thus, the inherent reactivity of the borane−water complex appears to be adequate for some synthetic conversions.

The borane−water complex should have a similar polar acceleration effect as observed in thiols, and this factor in

---

(27) Chatgilialoglu, C.; Dickhaut, J.; Giese, B. *J. Org. Chem.* **1991**, *56*, 6399−6403.

(28) Ha, C.; Horner, J. H.; Newcomb, M.; Varick, T. R.; Arnold, B. R.; Lusztyk, J. *J. Org. Chem.* **1993**, *58*, 1194−1198.

(29) Franz, J. A.; Bushaw, B. A.; Alnajjar, M. S. *J. Am. Chem. Soc.* **1989**, *111*, 268−275.

(30) Newcomb, M.; Choi, S. Y.; Horner, J. H. *J. Org. Chem.* **1999**, *64*, 1225−1231.

(31) Newcomb, M.; Varick, T. R.; Ha, C.; Manek, M. B.; Yue, X. *J. Am. Chem. Soc.* **1992**, *114*, 8158−8163.

(32) Kanabus-Kaminska, J. M.; Hawari, J. A.; Griller, D.; Chatgilialoglu, C. *J. Am. Chem. Soc.* **1987**, *109*, 5267−5268.

(33) Clark, K. B.; Griller, D. *Organometallics* **1991**, *10*, 746−750.

(34) Burkey, T. J.; Majewski, M.; Griller, D. *J. Am. Chem. Soc.* **1986**, *108*, 2218−2221.

(35) McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493−532.

(36) Berkowitz, J.; Ellison, G. B.; Gutman, D. *J. Phys. Chem.* **1994**, *98*, 2744−2765.

(37) Griller, D.; Kanabus-Kaminska, J. M.; Maccoll, A. *THEOCHEM* **1988**, *40*, 125−131.

(38) Janousek, B. K.; Reed, K. J.; Brauman, J. I. *J. Am. Chem. Soc.* **1980**, *102*, 3125−3129.

(39) Leeck, D. T.; Li, R. M.; Chyall, L. J.; Kenttamaa, H. I. *J. Phys. Chem.* **1996**, *100*, 6608−6611.

(40) Allen, R. P.; Roberts, B. P.; Willis, C. R. *J. Chem. Soc., Chem. Commun.* **1989**, 1387−1388.

combination with the computed small BDE[10] for the Me_3B-H_2O complex of 86 kcal/mol would lead to the prediction that hydrogen atom transfer trapping would be relatively efficient. In fact, the Et_3B-ROH complexes react less rapidly at room temperature than one might expect, apparently reflecting the high entropy demand of these reactions indicated in the variable temperature studies. The positive aspect of this reactivity effect is that one can expect large relative changes in product distributions as a function of reaction temperature, introducing a subtle method for controlling product yield.

One essential requirement for synthetic applications is that each step in the radical chain sequence is efficient, and that would limit the use of the borane−water complex to xanthates and related radical precursors and possibly alkyl iodides because an alkyl chloride or alkyl bromide will not react efficiently with an ethyl radical that is formed from the Et_3B-OH radical after H-atom reaction of the complex.[10] Such a limitation also exists for thiols because a thiyl radical will not abstract halogen from an alkyl halide. Nonetheless, thiols can be used with alkyl halides in a mixed reagent system comprised of a thiol as the H-atom donor and Et_3SiH, which reacts with the thiyl radical to give a silyl radical that propagates the chain with alkyl halides.[40] It is interesting to speculate that a similar mixed reagent system might permit the use of the borane−water complex as a H-atom donor when alkyl halide radical precursors are employed.

In summary, the room temperature rate constants for reactions of triethylborane complexes of water and methanol as H-atom donors to alkyl radicals are 2 orders of magnitude smaller than those for reactions of tin hydride reagents. These reactions are adequately fast at room temperature for some synthetic applications, and they are increasingly competitive with radical rearrangements at reduced temperatures. One anticipates increasing numbers of applications of borane complexes as radical reducing agents given the ease of removal of the boron-containing byproducts, especially if a mixed reagent system can be developed that permits the use of common alkyl halides as radical precursors.

Experimental Section

The syntheses of the xanthate ester from 2-decanol and radical precursors **2** and **7** and details for identifications of the products from their reactions are described in the Supporting Information. Yields were determined by analytical GC with thermal conductivity detection. In studies involving measurements of the percentage of deuterium in a product, GC−mass spectrometry with EI ionization and SIM mode data collection was employed.

Procedure for Kinetic Studies. In a typical reaction, xanthate precursor **7** (20 mg, 0.06 mmol) was dissolved in 3.4 mL of benzene, and 21.6 μL of D_2O (1.1 mmol) was added. The mixture was degassed by bubbling with nitrogen gas for 20 min. Et_3B (1.0 M in hexane, 1.21 mL, 1.2 mmol) was added to the mixture. The reaction mixture was stirred, and oxygen was introduced slowly via a bubbler. The reaction was continued until no starting material was observed by TLC analysis (ca. 6 h). The reaction mixture was passed through a small column containing silica gel with hexane elution. Tetradecane was added as an internal standard, and the mixture was analyzed by GC. The yields of products **10** and **11** were determined using measured response factors.

Variable Temperature Study. Xanthate radical precursor **7** (40 mg, 0.12 mmol) was dissolved in dry toluene (3.4 mL), and 49 μL of MeOH (1.2 mmol) was added. The mixture was degassed by bubbling with nitrogen gas for 20 min and equilibrated in a bath at the desired temperature. Et_3B (1.0 M in hexane, 1.21 mL, 1.2 mmol) was added to the mixture. The reaction mixture was stirred, and oxygen was introduced slowly via a bubbler. The reaction mixture was stirred, and the progress of the reaction was followed by TLC. Reactions at reduced temperature required extended reaction times (up to 24 h). The reaction mixture was passed through a small column containing silica gel with hexane elution, and the eluent was analyzed by GC to determine the ratio of acyclic product **10** to rearranged product **11**.

Acknowledgment. This work was supported by a grant from the National Science Foundation (CHE-0601857).

Supporting Information Available: Synthetic details, detailed kinetic results, and NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

JO070336S