

# Absolute rate constants for some reactions of the triethylamine-boryl radical and the borane radical anion

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Brad Sheeller and Keith U. Ingold

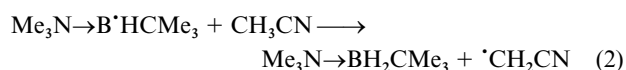
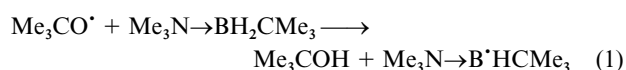
Steele Institute for Molecular Sciences, National Research Council of Canada,  
100 Sussex Drive, Ottawa, Ontario, Canada K1A 0R6

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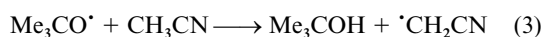
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Laser flash photolysis (LFP) of di-*tert*-butyl peroxide or dicumyl peroxide at ambient temperatures in the presence of  $\text{Et}_3\text{N}\rightarrow\text{BH}_3$  or  $\text{BH}_4^-$  generated the title radicals which were found to have broad, featureless absorptions in the visible region. Rate constants for H-atom abstraction from  $\text{Et}_3\text{N}\rightarrow\text{BH}_3$  by cumyloxyl radicals show a small solvent dependence, e.g.  $12 \times 10^7$  and  $2.2 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  in isooctane and acetonitrile, respectively. Rate constants for halogen atom abstraction by  $\text{Et}_3\text{N}\rightarrow\text{BH}_2^\cdot$  and  $\text{BH}_3^{\cdot-}$  from a number of chlorides and bromides were determined by LFP and by competitive kinetics, e.g., for  $\text{Et}_3\text{N}\rightarrow\text{BH}_2^\cdot + \text{CCl}_4/\text{PhCH}_2\text{Cl}/\text{CH}_3(\text{CH}_2)_2\text{Cl}$ ,  $k = 4.4 \times 10^9/1.1 \times 10^7/5.1 \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  and for  $\text{BH}_3^{\cdot-} + \text{CCl}_4/\text{PhCH}_2\text{Cl}$ ,  $k = 2.0 \times 10^9/3.0 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . Rates of addition of  $\text{Et}_3\text{N}\rightarrow\text{BH}_2^\cdot$  to 1- and 1,1-substituted olefins increase dramatically as the electron affinity of the olefin increases, confirming the nucleophilic character of amine-boryl radicals. A comparison of the present results with literature data for the addition of olefins of four nucleophilic carbon-centered radicals proves that  $\text{Et}_3\text{N}\rightarrow\text{BH}_2^\cdot$  is by far the most nucleophilic radical for which kinetic data are available. A few rate constants for abstraction of hydrogen from electron-deficient carbon by  $\text{Et}_3\text{N}\rightarrow\text{BH}_2^\cdot$  are also reported.

In a major series of publications that began almost 20 years ago, Roberts and co-workers have shown that the borane radical anion,  $\text{BH}_3^{\cdot-}$ ,<sup>1,2</sup> and amine-boryl radicals, e.g.,  $\text{Et}_3\text{N}\rightarrow\text{BH}_2^\cdot$ ,<sup>3,4</sup> and related species, exhibit some fascinatingly “different” homolytic chemistry from that of more familiar radicals such as alkoxy and trialkyltins. Amine-boryl radicals are strongly nucleophilic. For this reason, and because the reactions are exothermic, amine-boryl radicals can abstract hydrogen atoms from very electron-deficient C–H bonds such as those in acetonitrile<sup>5</sup> and from C–H groups  $\alpha$  to carbonyl substituents in esters, lactones and related compounds.<sup>6,7</sup> These types of C–H groups donate H-atoms very reluctantly when under attack by (electrophilic) alkoxy radicals, which are the radicals normally employed to abstract hydrogen from C–H bonds. However, alkoxy radicals do react readily with amine-borane complexes to yield amine-boryl radicals. These kinetic “oddities” have been exploited and developed by Roberts, who has christened the phenomenon “polarity reversal catalysis” (PRC).<sup>5–8</sup> For example,<sup>5</sup> the cyanomethyl radical can be generated from acetonitrile by reactions (1) and (2):



Sterically non-hindered amine-boryl radicals, such as  $\text{Et}_3\text{N}\rightarrow\text{BH}_2^\cdot$ , add to acetonitrile<sup>5</sup> but sterically hindered  $\text{Me}_3\text{N}\rightarrow\text{B}^\cdot\text{HR}$  radicals are true catalysts for the otherwise very slow reaction (3).



PRC has been developed further into synthetically useful chain reactions (with the chains being carried by amine-boryl and *tert*-butoxy radicals)<sup>8,9</sup> and into enantioselective H-atom abstractions using chiral amine-boryl radicals.<sup>10–12</sup>

Amine-boryl radicals and the borane radical anion can also abstract halogen atoms from alkyl halides,<sup>2–5,7,13–15</sup> add to olefins, aromatics and other unsaturated compounds,<sup>2,4,5,13,16</sup> and generally do chemistry reminiscent of silicon- and tin-centered radical chemistry, though with different selectivities.

It is well recognized that a knowledge of the potentially relevant absolute rate constants for radical reactions is a great asset for synthetic planning.<sup>17</sup> Nevertheless, and despite the unique properties and versatility of amine-boryl radicals, there are remarkably few kinetic data of any kind available, including, in particular, data at room temperature which could prove useful to synthetic chemists. To remedy this situation, we have applied the technique of laser flash photolysis (LFP) to determine absolute rate constants for the formation (*via* alkoxy radicals) and some reactions of  $\text{Et}_3\text{N}\rightarrow\text{BH}_2^\cdot$  and  $\text{BH}_3^{\cdot-}$  at room temperature.

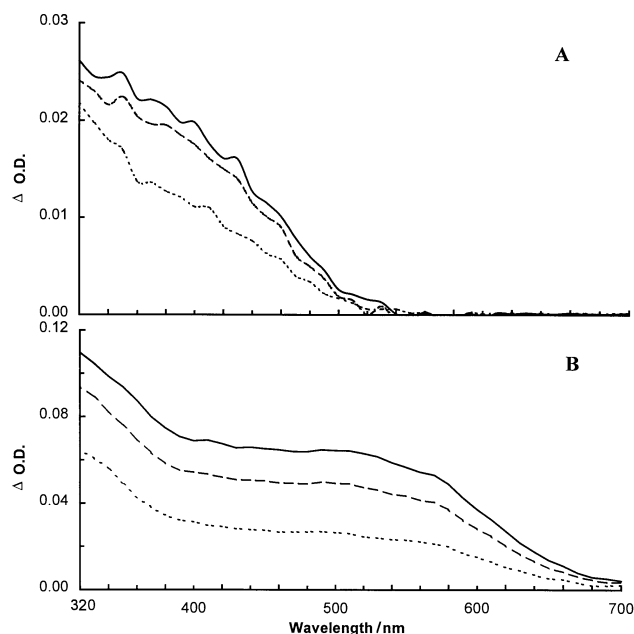
## Results

### UV–Visible spectra of $\text{Et}_3\text{N}\rightarrow\text{BH}_2^\cdot$ and $\text{BH}_3^{\cdot-}$

LFP (308 nm) of di-*tert*-butyl peroxide (4%)–benzene solutions containing  $\text{Et}_3\text{N}\rightarrow\text{BH}_3$  (44 mM) or *n*-Bu<sub>4</sub>N<sup>+</sup>BH<sub>4</sub><sup>–</sup> (24 mM) yielded the spectra (recorded at 10 nm intervals from 320 to 600 nm) shown in Figs. 1A and 1B, which are assigned to  $\text{Et}_3\text{N}\rightarrow\text{BH}_2^\cdot$  and  $\text{BH}_3^{\cdot-}$ , respectively. Although these spectra are almost featureless, they do allow kinetic data for reactions of these two radicals with added substrates to be derived even when the substrate-derived radical has no absorption in the visible or near UV regions of the spectrum.

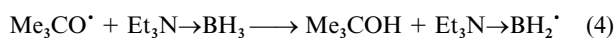
### Kinetics of the reactions of *tert*-alkoxy radicals with $\text{Et}_3\text{N}\rightarrow\text{BH}_3$ and $\text{BH}_4^-$

The absolute rate constants for H-atom abstraction from these two substrates in benzene were measured by LFP using 4% (v/v) di-*tert*-butyl peroxide and 0.12 M dicumyl peroxide, the peroxide concentrations being chosen to give an absorbance of ca. 0.3 at the 308 nm laser wavelength in the 7 × 7 mm<sup>2</sup> quartz LFP

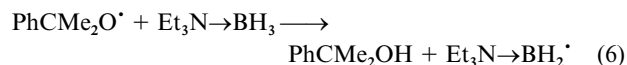


**Fig. 1** Transient absorption spectra of  $\text{Et}_3\text{N}\rightarrow\text{BH}_2^*$  (A) and  $\text{BH}_3^{\cdot-}$  (B) in di-*tert*-butyl peroxide–benzene (4 : 96, v/v) measured for  $\text{Et}_3\text{N}\rightarrow\text{BH}_2^*$  1.2 (—), 4.4 (---) and 6.4 ( $\cdots$ )  $\mu\text{s}$  and for  $\text{BH}_3^{\cdot-}$  4.4 (—), 8.0 (---) and 16.0 ( $\cdots$ )  $\mu\text{s}$  after the laser pulse.

cell. The alkoxy radicals are generated “instantaneously” in the laser pulse. Because *tert*-butoxy radicals have no absorption in the near UV–visible,<sup>18</sup> the pseudo-first-order grow-ins,  $k_{\text{exptl}}$ , of the absorptions due to  $\text{Et}_3\text{N}\rightarrow\text{BH}_2^*$  and  $\text{BH}_3^{\cdot-}$  [reactions (4) and (5)] were monitored at 375 nm and 475 nm, respectively.



However, cumyloxy radicals have a fairly strong absorption in the visible,  $\lambda_{\text{max}} = 485 \text{ nm}$ ,<sup>18</sup> and in this case the pseudo-first-order decay ( $k_{\text{exptl}}$ ) of cumyloxy [reactions (6) and (7)] was monitored.



Measurements of  $k_{\text{exptl}}$  were made over a range of  $\text{Et}_3\text{N}\rightarrow\text{BH}_3$  and  $\text{BH}_4^-$  concentrations. The desired second-order rate constants,  $k_n$  ( $n = 4\text{--}7$ ) were obtained from plots of  $k_{\text{exptl}}$  vs. [substrate], all of which gave excellent straight lines ( $r^2 \geq 0.97$ ), *via* relation (8),

$$k_{\text{exptl}} = k_0 + k_n[\text{substrate}] \quad (8)$$

where  $k_0$  represents all first-order and pseudo-first-order processes other than the alkoxy radical/substrate reaction.

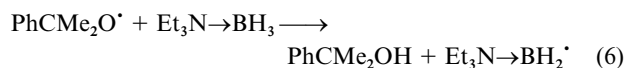
It has been commonly assumed that all *tert*-alkoxy radicals have equal reactivities in H-atom abstractions. We have now found that this assumption is not completely accurate. In benzene for H-atom abstraction from  $\text{Et}_3\text{N}\rightarrow\text{BH}_3$ :  $k_4 = (5.3_4 \pm 0.06) \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  (mean of four experiments,  $\pm 1 \sigma$ ) and  $k_6 = (4.0_1 \pm 0.08) \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  (mean of two experiments,  $\pm 1 \sigma$ ). Similarly, in benzene for H-atom abstraction from  $\text{BH}_4^-$ :  $k_5 = (6.1_7 \pm 0.09) \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  and  $k_7 = (5.2 \pm 0.1) \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  (mean of two experiments,  $\pm 1 \sigma$ ).

#### Kinetic solvent effects (KSEs) on reaction (6)

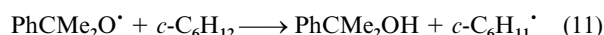
There are no significant KSEs for H-atom abstraction from saturated hydrocarbons (such as cyclohexane)<sup>19</sup> because they are not hydrogen bond donors, HBDs.<sup>20</sup> However, there are

very large KSEs in hydrogen bond accepting (HBA) solvents for H-atom abstractions from substrates such as *tert*-butyl hydroperoxide, phenol and  $\alpha$ -tocopherol, which are fairly strong HBDs.<sup>20–22</sup> Rate constants for H-atom abstraction from such hydroxylic substrates,  $k_{\text{XOH/Y}}^{\text{S}}$ , decrease as the solvent, S, becomes a stronger HBA and, in fact, for each XOH substrate there is a linear correlation between  $\log k_{\text{XOH/Y}}^{\text{S}}$  and Abraham *et al.*'s<sup>23</sup>  $\beta_2^{\text{H}}$  scale of solvent HBA abilities.<sup>20,24</sup> Although the borohydric hydrogen atoms of  $\text{Et}_3\text{N}\rightarrow\text{BH}_3$  are expected to be very poor HBDs (implying negligible KSEs resulting from hydrogen bonding) solvent effects on reaction (6) seemed worth investigating because Lucarini *et al.*<sup>25</sup> had reported that  $k_4$  is 5 times larger in pyridine than in *tert*-butylbenzene. Since pyridine ( $\beta_2^{\text{H}} = 0.62$ )<sup>23</sup> is a much stronger HBA than *tert*-butylbenzene (for which  $\beta_2^{\text{H}}$  has not been reported but is probably similar to toluene,  $\beta_2^{\text{H}} = 0.14$ )<sup>23</sup> the results of Lucarini *et al.* would imply that  $k_4$  (and  $k_6$ ) increase in magnitude as the solvent becomes more polar, presumably by stabilizing a highly polar transition state (as is the case for H-atom abstraction from reduced glutathione, RSH, by a tertiary alkyl radical).<sup>26</sup>

The results of our LFP direct measurements of  $k_6$  in 10 solvents are given in Table 1. Unfortunately, pyridine absorbs too strongly at the laser wavelength to be used as a solvent in LFP experiments. We therefore generated cumyloxy radicals by the thermal decomposition of dicumyl hyponitrite at 25 °C in the dark<sup>20</sup> in pyridine containing 7 different concentrations of  $\text{Et}_3\text{N}\rightarrow\text{BH}_3$  and after 10 days (15 half-lives of the hyponitrite) measured the relative yields of cumyl alcohol and acetophenone [reactions (9), (6) and (10)]:



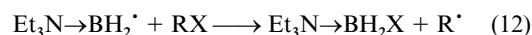
A plot of  $[\text{PhCMe}_2\text{OH}]/[\text{PhCOMe}]$  vs.  $[\text{Et}_3\text{N}\rightarrow\text{BH}_3]$  gave an excellent straight line ( $r^2 = 1.00$ ) the slope of which yields  $k_6/k_{10} = 92 \text{ dm}^3 \text{ mol}^{-1}$ . Since  $k_{10}$  varies with solvent,<sup>19</sup> its magnitude was determined in pyridine using cyclohexane as the H-atom donor because H-atom abstraction from cyclohexane is known to be solvent independent [reaction (11)].<sup>19</sup>



Analyses of alcohol : acetophenone ratios at various  $[c\text{-C}_6\text{H}_{12}]$  also gave an excellent straight line ( $r^2 = 1.00$ ) with a slope which yields  $k_{11}/k_{10} = 3.8 \text{ dm}^3 \text{ mol}^{-1}$ . Since  $k_{11} = 1.2 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ,<sup>19</sup> we obtain  $k_{10} = 3.2 \times 10^5 \text{ s}^{-1}$  and, hence,  $k_6$  (pyridine) =  $2.9 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . This value is listed in Table 1 after the data for the 10 solvents in which the reaction was studied by LFP.

#### Halogen atom abstraction by $\text{Et}_3\text{N}\rightarrow\text{BH}_2^*$ and $\text{BH}_3^{\cdot-}$

LFP of 6% (v/v) di-*tert*-butyl peroxide–benzene containing 0.14 M  $\text{Et}_3\text{N}\rightarrow\text{BH}_3$  or 0.02 M  $\text{BH}_4^-$  generated the corresponding boron-centered radicals “instantaneously”. The decay of these radicals was monitored directly in the presence of at least 5 different concentrations of various alkyl chlorides and bromides to obtain  $k_{12}$  and  $k_{13}$  from reactions (12) and (13) (see Table 2).



For R = benzyl the grow-in of the benzyl radical was also monitored (at 321 nm) giving, as expected, the same rate constants (within experimental error) as were obtained from decay of the boron-centered radicals (see footnotes *e, f, i* and *k* in Table 2).

The LFP technique could only be used with halides which were as reactive as *tert*-butyl chloride or more reactive. The scale of halide reactivities towards  $\text{Et}_3\text{N}\rightarrow\text{BH}_2^\cdot$  radicals was therefore extended by competitive experiments involving *n*-propyl bromide and an alkyl chloride with analyses for  $\text{Et}_3\text{N}\rightarrow\text{BH}_2\text{Br}/\text{Et}_3\text{N}\rightarrow\text{BH}_2\text{Cl}$  ratios by  $^{11}\text{B}$  NMR. This analytical procedure was first checked using benzyl chloride and *tert*-butyl chloride. The rate constants calculated from the competition experiments were in excellent agreement with the directly measured rate constants (see second entry for each of these halides in Table 2).

#### Addition reactions of $\text{Et}_3\text{N}\rightarrow\text{BH}_2^\cdot$

Rate constants for addition of the  $\text{Et}_3\text{N}\rightarrow\text{BH}_2^\cdot$  radical to some unsaturated molecules were measured in benzene by monitor-

**Table 1** Ambient temperature absolute rate constants for H-atom abstraction from  $\text{Et}_3\text{N}\rightarrow\text{BH}_3$  by cumyloxy radicals in various solvents and the empirical parameters  $\beta_2^{\text{H}}$  and  $E_T(30)$ , which reflect certain properties of those solvents

Solvent	$10^{-7} k/\text{dm}^3 \text{mol}^{-1} \text{s}^{-1a}$	$\beta_2^{\text{H}b}$	$E_T(30)^c$
1. Isooctane	12 ± 1	0.00	31.0
2. $\text{CCl}_4$	8.8 ± 0.1	0.05 <sup>d</sup>	32.4
3. <i>tert</i> -Butylbenzene	7.9 ± 0.2	0.14 <sup>e</sup>	33.9 <sup>e</sup>
4. <i>tert</i> -Butyl alcohol	7.1 ± 0.1	0.49	43.3
5. Benzene	4.0 ± 0.1 <sup>f</sup>	0.14	34.3
6. Ethyl acetate	3.7 ± 0.2	0.45	38.1
7. DMSO	3.2 ± 0.1	0.78	45.1
8. Methyl acetate	3.0 ± 0.2	0.40	40.0
9. Methyl formate	2.6 ± 0.3	0.38	45.0
10. Acetonitrile	2.2 ± 0.1	0.44	45.6
11. Pyridine	2.9 ± 0.1 <sup>g</sup>	0.62	40.5

<sup>a</sup>Average *k* from two separate sets of experiments with 1σ errors as determined by monitoring the pseudo-first order decay of LFP generated cumyloxy radicals using five or more  $\text{Et}_3\text{N}\rightarrow\text{BH}_3$  concentrations, unless otherwise noted. <sup>b</sup>Ref. 23 unless otherwise noted. <sup>c</sup>Units are kcal mol<sup>-1</sup>, ref. 39. <sup>d</sup>Ref. 20. <sup>e</sup>Not available, therefore assumed to be the same as for toluene. <sup>f</sup>Average of four separate sets of experiments. <sup>g</sup>Calculated from plots of [cumyl alcohol]/[acetophenone] vs. [ $\text{Et}_3\text{N}\rightarrow\text{BH}_3$ ], the cumyloxy radicals being generated by thermal decomposition of dicumyl hyponitrite (see text).

ing the pseudo-first-order decay of  $\text{Et}_3\text{N}\rightarrow\text{BH}_2^\cdot$  (see Table 3). For phenylacetylene and acetonitrile any addition (or other reaction) was too slow to measure by LFP (*i.e.*,  $\leq 5 \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ). Chlorinated olefins were excluded from this study because LFP measures only “global” rate constants and reaction with, for example,  $\text{H}_2\text{C}=\text{CCl}_2$  was shown by  $^{11}\text{B}$  NMR to occur, at least to some extent, by chlorine atom abstraction.

#### Hydrogen atom abstraction from electron-deficient C–H groups by $\text{Et}_3\text{N}\rightarrow\text{BH}_2^\cdot$

These reactions are important for PRC. However, we found only three substrates which were sufficiently reactive to measure absolute rate constants,  $k_{14}$ , by LFP and monitor the decay of  $\text{Et}_3\text{N}\rightarrow\text{BH}_2^\cdot$  in reaction (14) (EWG = electron withdrawing

**Table 3** Ambient temperature absolute rate constants for addition of  $\text{Et}_3\text{N}\rightarrow\text{BH}_2^\cdot$  radicals to some unsaturated substrates in benzene

Substrate	EA/eV <sup>a</sup>	$10^{-6} k/\text{dm}^3 \text{mol}^{-1} \text{s}^{-1b}$
1. $\text{C}_6\text{F}_5\text{CH}=\text{CH}_2$	0.51 <sup>c</sup>	240 ± 50
2. $(\text{C}_6\text{H}_5)_2\text{C}=\text{CH}_2$	0.36 <sup>d</sup>	320 ± 40
3. $\text{C}_6\text{H}_5\text{CMe}=\text{CH}_2$	-0.23	41 ± 4
4. $\text{C}_6\text{H}_5\text{CH}=\text{CH}_2$	-0.25	110 ± 60
5. $\text{MeOC(O)CMe}=\text{CH}_2$	-0.38 <sup>d</sup>	170 ± 50
6. $\text{MeOC(O)CH}=\text{CH}_2$	-0.49	540 ± 30
7. $(\text{EtO})_3\text{SiCH}=\text{CH}_2$	-1.11	6.3 ± 0.6
8. $\text{Me}_3\text{SiCH}=\text{CH}_2$	-1.14	2.1 ± 0.4
9. $\text{MeCO}_2\text{CH}=\text{CH}_2$	-1.19	2.5 ± 0.4
10. $\text{N}\equiv\text{CCH}_2\text{CH}=\text{CH}_2$	-1.31	2.2 ± 0.4
11. $\text{HOCH}_2\text{CH}=\text{CH}_2$	-1.49	1.1 ± 0.3
12. $\text{MeCO}_2\text{CMe}=\text{CH}_2$	-1.51	1.2 ± 0.3
13. $\text{C}_6\text{H}_5\text{CH}_2\text{CH}=\text{CH}_2$	-1.66	<0.5
14. $\text{Me}_3\text{CCH}=\text{CH}_2$	-1.73	<0.5
15. $\text{EtOCH}=\text{CH}_2$	-2.24	<0.5
16. $\text{MeOCMe}=\text{CH}_2$	-2.48	<0.5
$\text{C}_6\text{H}_5\text{CH}=\text{CHCH}_3$		2.3 ± 0.5
$\text{C}_6\text{H}_5\text{C}\equiv\text{N}$		7.0 ± 0.3

<sup>a</sup>From ref. 36 unless otherwise noted. <sup>b</sup>Average *k* from two separate sets of experiments with 1σ errors as determined by monitoring the decay of  $\text{Et}_3\text{N}\rightarrow\text{BH}_2^\cdot$ . <sup>c</sup>Not available. Value is based on theoretical calculations (see text). <sup>d</sup>From ref. 34.

**Table 2** Ambient temperature absolute rate constants for some halogen atom abstractions by  $\text{Et}_3\text{N}\rightarrow\text{BH}_2^\cdot$  and  $\text{BH}_3^{\cdot-}$  radicals in benzene (plus related data from the literature for trialkylsilicon-, germanium- and tin-centered radicals)

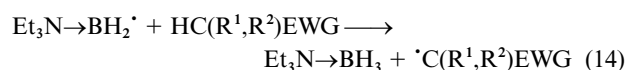
Halide	$10^{-6} k/\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$				
	$\text{Et}_3\text{N}\rightarrow\text{BH}_2^\cdot^a$	$\text{BH}_3^{\cdot-}^a$	$\text{Et}_3\text{Si}^\cdot^b$	$\text{Bu}_3\text{Ge}^\cdot^c$	$\text{Bu}_3\text{Sn}^\cdot^d$
$\text{CCl}_4$	4400 ± 300	2000 ± 300	4600	310	—
$\text{CHCl}_3$	3300 ± 500	620 ± 30	250	—	—
$\text{PhCH}_2\text{Br}$	1700 ± 200 <sup>e</sup>	530 ± 40 <sup>f</sup>	2400	790	1500 <sup>g</sup>
$(\text{CH}_3)_3\text{CBr}$	230 ± 20	320 ± 20	1100	86	145 (170) <sup>c</sup>
<i>c</i> - $\text{C}_6\text{H}_{11}\text{Br}$	150 ± 20	200 ± 30	—	—	37
$\text{CH}_3(\text{CH}_2)_2\text{Br}$	130 ± 20	170 ± 20	1500 <sup>h</sup>	46	32 <sup>i</sup> (26) <sup>c</sup>
$\text{CH}_2\text{Cl}_2$	120 ± 20	110 ± 20	71	—	—
$\text{PhCH}_2\text{Cl}$	11 ± 4 <sup>j</sup>	30 ± 5 <sup>k</sup>	20	1.9	1.1
$\text{PhCH}_2\text{Cl}$	13 ± 3 <sup>l</sup>	—	—	—	—
$(\text{CH}_3)_3\text{CCl}$	1.2 ± 0.3	—	2.5	<0.05	0.027
$(\text{CH}_3)_3\text{CCl}$	1.4 ± 0.4 <sup>l</sup>	—	—	—	—
<i>c</i> - $\text{C}_6\text{H}_{11}\text{Cl}$	0.43 ± 0.08 <sup>l</sup>	—	—	—	0.0034
$\text{CH}_3(\text{CH}_2)_2\text{Cl}$	0.51 ± 0.08 <sup>lm</sup>	—	0.31 <sup>g</sup>	—	0.0015 <sup>i</sup>

<sup>a</sup>Average *k* from two separate sets of experiments as determined by monitoring decay of the boron-centered radical using five or more halide concentrations, unless otherwise noted. Values determined by monitoring the grow-in of the benzyl radical product,  $k_{\text{grow}}$ , are given in footnotes. <sup>b</sup>C. Chatgililoglu, K. U. Ingold and J. C. Scaiano, *J. Am. Chem. Soc.*, 1982, **104**, 5123. <sup>c</sup>K. U. Ingold, J. Luszyk and J. C. Scaiano, *J. Am. Chem. Soc.*, 1984, **106**, 343. <sup>d</sup>D. J. Carlsson and K. U. Ingold, *J. Am. Chem. Soc.*, 1968, **90**, 7047. However, the originally reported constants have been multiplied by a factor of 1.7, see footnote *d* to Table III in the reference cited in footnote *c* of the present table. <sup>e</sup> $k_{\text{grow}} = (1600 \pm 500) \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . <sup>f</sup> $k_{\text{grow}} = (510 \pm 50) \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . <sup>g</sup>M. Anpo, R. Sutcliffe and K. U. Ingold, *J. Am. Chem. Soc.*, 1983, **105**, 3580. Reported value multiplied by 1.7. <sup>h</sup>*n*-Butyl halide. <sup>i</sup>*n*-Pentyl halide. <sup>j</sup> $k_{\text{grow}} = (10 \pm 5) \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . <sup>k</sup> $k_{\text{grow}} = (27 \pm 6) \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . <sup>l</sup>Competitive experiment with  $\text{CH}_3(\text{CH}_2)_2\text{Br}$  analyzed by  $^{11}\text{B}$  NMR. <sup>m</sup>For *n*-butyl chloride  $k = (0.48 \pm 0.07) \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ .

**Table 4** Ambient temperature absolute rate constants for hydrogen atom abstraction from some electron-deficient C–H bonds by  $\text{Et}_3\text{N}\rightarrow\text{BH}_2^{\cdot}$  in benzene

Substrate	$10^{-6} k_4 / \text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ <sup>a</sup>	Reactivities relative to $n\text{-PrBr} = 100$	
		$\text{Et}_3\text{N}\rightarrow\text{BH}_2^{\cdot}$ <sup>b</sup>	$\text{Me}_3\text{N}\rightarrow\text{B}^{\cdot}\text{HCMe}_2\text{CHMe}_2$ <sup>c</sup>
$\text{HC}(\text{CO}_2\text{Et})_3$	$33 \pm 3$	16.5	19
$\text{H}_2\text{C}(\text{CO}_2\text{Et})_2$	$12 \pm 4$	6.0	6.6
$\text{H}(\text{CH}_3)\text{C}(\text{CO}_2\text{Et})_2$	$2.2 \pm 0.3$	1.1	0.3
$(\text{CH}_2\text{CO}_2\text{Et})_2$	$\leq 0.5$ <sup>d</sup>	—	0.03
$\text{H}_3\text{CCO}_2\text{Et}$	$\leq 0.5$ <sup>d</sup>	—	0.002

<sup>a</sup> Average  $k$  from two separate sets of experiments as determined by monitoring the decay of  $\text{Et}_3\text{N}\rightarrow\text{BH}_2^{\cdot}$  at five or more ester concentrations. <sup>b</sup> This work. <sup>c</sup> At 189 K, ref. 6. <sup>d</sup> Too slow to measure.



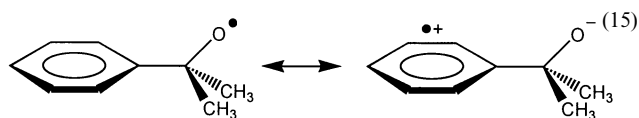
group) (see Table 4). The known<sup>7</sup> reaction (of  $\text{Me}_3\text{N}\rightarrow\text{BH}_2^{\cdot}$ ) with ethyl acetate, for example, was too slow to measure.

Hydrogen atom abstractions by  $\text{BH}_3^{\cdot-}$  from all the H-atom donors listed in Table 4 were too slow to measure, *i.e.*,  $k \leq 5 \times 10^5 \text{ dm}^3 \text{mol}^{-1} \text{s}^{-1}$ .

## Discussion

The extensive, low temperature, EPR studies of Roberts and co-workers<sup>1–16</sup> leave no doubt that the initial, *i.e.*, kinetic, products of the reaction of *tert*-alkoxyl radicals with amine-boranes and the borohydride anion are amine-boryl radicals and the borane radical anion, respectively. Since our measurements of absolute rate constants are based mainly on monitoring the decay of the transient absorptions shown in Figs. 1A and B, and since these kinetic data are fully congruent with the results of the EPR experiments, we unhesitatingly assign these spectra to  $\text{Et}_3\text{N}\rightarrow\text{BH}_2^{\cdot}$  and  $\text{BH}_3^{\cdot-}$ , respectively.

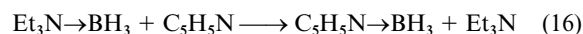
The slightly lower reactivity of cumyloxyl in H-atom abstraction from these two boranes (*ca.* 80%) compared with *tert*-butoxyl was unexpected, since it has been tacitly assumed that these two alkoxy radicals are equally reactive. The lower reactivity of cumyloxyl could arise from several causes, *e.g.* greater steric hindrance of the radical center, the inductive effect of the phenyl group, *etc.* However, it is tempting to attribute it to a lower spin density on oxygen in cumyloxyl relative to *tert*-butoxyl, which is a consequence of the internal charge transfer (15) that gives rise to cumyloxyl's visible absorption band.<sup>18</sup>



The borohydride anion is about 10 times as reactive as triethylamine-borane towards *tert*-alkoxyl radicals in benzene at room temperature, *e.g.*,  $k_7 = 5.2 \times 10^8 \text{ dm}^3 \text{mol}^{-1} \text{s}^{-1}$  and  $k_6 = 4.0 \times 10^7 \text{ dm}^3 \text{mol}^{-1} \text{s}^{-1}$ . We are not aware of any earlier work on the kinetics of the former reaction. However, for the latter reaction, Lucarini *et al.*<sup>25</sup> reported  $k_4 = 2.6 \times 10^7$  and  $13 \times 10^7 \text{ dm}^3 \text{mol}^{-1} \text{s}^{-1}$  at 25 °C in *tert*-butylbenzene and pyridine respectively.† These workers used a competitive kinetic procedure. *tert*-Butoxyl radicals were generated by photolysis

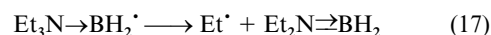
† The rate constant for the reaction:  $\text{Me}_3\text{CO}^{\cdot} + \text{Me}_3\text{CMe}_2\text{N}\rightarrow\text{BH}_3 \longrightarrow \text{Me}_3\text{COH} + \text{Me}_3\text{CMe}_2\text{N}\rightarrow\text{BH}_2^{\cdot}$ , has been estimated *via* EPR competition experiments to be  $2.9 \times 10^7 \text{ dm}^3 \text{mol}^{-1} \text{s}^{-1}$  in cyclopropane-oxirane at 282 K,<sup>47</sup> a result congruent with our measurements of  $k_4$  at *ca.* 296 K.

of di-*tert*-butyl peroxide in the presence of  $\text{Et}_3\text{N}\rightarrow\text{BH}_3$  and  $\text{Ph}_3\text{SiH}$  or  $(\text{Me}_3\text{Si})_3\text{SiH}$ . Since the rate constants for H-atom abstraction by *tert*-butoxyl radicals from the two silanes are known, a determination of the relative consumption of  $\text{Et}_3\text{N}\rightarrow\text{BH}_3$  and the silane yielded  $k_4$ . The value they obtained for  $k_4$  in *tert*-butylbenzene ( $2.6 \times 10^7$ ) is in fair agreement with our directly-measured value of  $7.9 \times 10^7 \text{ dm}^3 \text{mol}^{-1} \text{s}^{-1}$  (Table 1). However, their value in pyridine ( $13 \times 10^7$ ) appeared to be anomalous because our results showed that  $k_6$  decreased in more polar solvents (Table 1) rather than increased. Since direct measurement of  $k_4$  or  $k_6$  by LFP was not possible in pyridine we carried out a competition between H-atom abstraction from  $\text{Et}_3\text{N}\rightarrow\text{BH}_3$  by the cumyloxyl radical (yielding cumyl alcohol) and  $\beta$ -scission of cumyloxyl (yielding acetophenone). This procedure gave  $k_6 = 2.9 \times 10^7 \text{ dm}^3 \text{mol}^{-1} \text{s}^{-1}$  in pyridine, which is a factor of 4.5 lower than Lucarini *et al.*'s estimate of  $k_4$ . However, as these authors recognized, there is always the potential for ligand exchange when an aliphatic amine-borane is dissolved in pyridine. They demonstrated (by GC) that such exchange was unimportant on the short (15–30 min) time scale of their experiments.<sup>25</sup> Exchange becomes much more likely on our time scale (50% reaction in 16 h). We therefore used <sup>11</sup>B NMR to monitor reaction (16) in neat pyridine at room

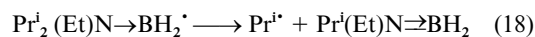


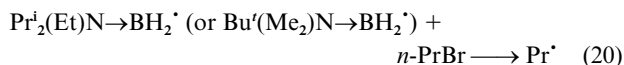
temperature. The half-life for formation of  $\text{C}_5\text{H}_5\text{N}\rightarrow\text{BH}_3$  was found to be 50 h. Clearly, the major reaction monitored in our experiments in pyridine was hydrogen atom abstraction from  $\text{Et}_3\text{N}\rightarrow\text{BH}_3$ , not abstraction from  $\text{C}_5\text{H}_5\text{N}\rightarrow\text{BH}_3$ . This conclusion is consistent with our kinetic results, which show that hydrogen abstraction (from  $\text{Et}_3\text{N}\rightarrow\text{BH}_3$ ) is *slower* in pyridine than in *tert*-butylbenzene. That is, the B–H bonds in  $\text{C}_5\text{H}_5\text{N}\rightarrow\text{BH}_3$  would be expected to be slightly weaker than those in  $\text{Et}_3\text{N}\rightarrow\text{BH}_3$  because of delocalization of the unpaired electron in  $\text{C}_5\text{H}_5\text{N}\rightarrow\text{BH}_2^{\cdot}$  into the pyridine ring. Hydrogen atom abstraction would therefore be expected to be faster from the pyridine complex than from the triethylamine complex. We believe, that our rate constant ( $k_6$ ), is probably more reliable than Lucarini's ( $k_4$ ) because relative rate constant measurements made in competitive kinetic experiments are intrinsically less accurate when reactant loss is monitored (as in ref. 25) than when product formation is followed (as in our work). Moreover, our rate constant in pyridine is consistent with the trend observed in the LFP experiments which show that  $k_6$  decreases as the solvents become more polar.

Although the  $\text{Et}_3\text{N}\rightarrow\text{BH}_2^{\cdot}$  radical reacts extremely rapidly with some of the solvents listed in Table 1 (*e.g.*,  $\text{CCl}_4$ , see Table 2) this does not interfere with measurements of  $k_6$  because these are based on rates of decay of the cumyloxyl radicals as a function of  $[\text{Et}_3\text{N}\rightarrow\text{BH}_3]$ . In fact,  $\text{Et}_3\text{N}\rightarrow\text{BH}_2^{\cdot}$  decays quite rapidly and with first-order kinetics even in isooctane ( $k_{\text{decay}} = 1.7 \times 10^6 \text{ s}^{-1}$ ), in benzene ( $k_{\text{decay}} = 5.8 \times 10^5 \text{ s}^{-1}$ ) and in perdeuterobenzene ( $k_{\text{decay}} = 5.8 \times 10^5 \text{ s}^{-1}$ ) presumably mainly, or entirely, *via*  $\beta$ -scission [reaction (17)].



The potential alternative of H-atom abstraction in isooctane was essentially eliminated by showing that the rate constant for  $\text{Et}_3\text{N}\rightarrow\text{BH}_2^{\cdot}$  decay was identical in *c*- $\text{C}_6\text{H}_{12}$  and *c*- $\text{C}_6\text{D}_{12}$  ( $k_{\text{decay}} = 1.7 \times 10^6 \text{ s}^{-1}$ ) and is also identical to its value in isooctane. Analogous  $\beta$ -scission reactions have been shown by Roberts and co-workers<sup>4,27</sup> using EPR spectroscopy to be facile processes even at considerably lower temperatures. For example, in the competitions (18) or (19) *vs.* (20),  $k_{18}/k_{20} = 0.03$

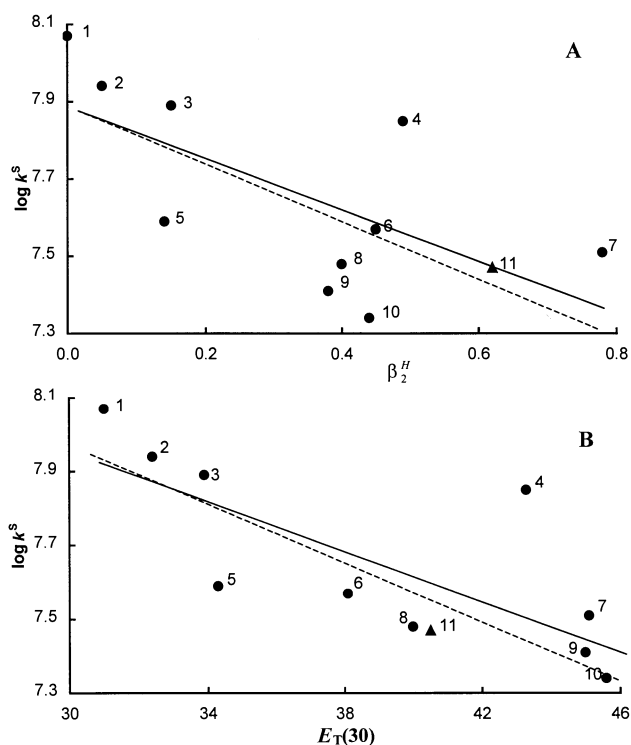




and  $k_{19}/k_{20} = 0.05 \text{ mol dm}^{-3}$  at 255 K.<sup>4</sup> Reactions (18) and (19) have also been monitored directly by time-resolved EPR spectroscopy over a range of temperatures.<sup>27</sup> It can be calculated from the Arrhenius parameters that at 25 °C,  $k_{18} = 6.3 \times 10^6 \text{ s}^{-1}$  and  $k_{19} = 1.6 \times 10^7 \text{ s}^{-1}$  in the solvent mixtures employed (cyclopropane, *tert*-alcohols and di-*tert*-butyl peroxide). These two  $\beta$ -scission rate constants are consistent with our measured rate constant for decay of  $\text{Et}_3\text{N} \rightarrow \text{BH}_2^{\cdot}$  in isooctane and benzene corresponding also to a  $\beta$ -scission, reaction (17). That is,  $\beta$ -scission is expected to become slower as the expelled radical changes from a tertiary, to a secondary, to a primary alkyl. Furthermore, because  $\text{R}_3\text{N} \rightarrow \text{BH}_2^{\cdot}$  radicals have large dipole moments (5.3 D calculated<sup>28</sup> for  $\text{Et}_3\text{N} \rightarrow \text{BH}_2^{\cdot}$ , *cf.* 5.7 D for  $\text{H}_3\text{N} \rightarrow \text{BH}_2^{\cdot}$ <sup>13</sup>) which are larger than those of the  $\text{R}_2\text{N} \rightarrow \text{BH}_2$  product (2.0 D calculated<sup>28</sup> for  $\text{Et}_2\text{N} \rightarrow \text{BH}_2$ ), the rate constants for  $\beta$ -scission of amine-boryl radicals are expected to be greatest in saturated hydrocarbon solvents and to decrease as the solvent becomes more polar.

The effect of solvents on the rate constants for H-atom abstraction from  $\text{Et}_3\text{N} \rightarrow \text{BH}_3$  by cumyloxy radicals correlate rather poorly with Abraham's<sup>23</sup>  $\beta_2^{\text{H}}$  (HBA accepting) parameter (see Fig. 2A, the least squares line yields  $r^2 = 0.45$ , or 0.58 if the point for *tert*-butyl alcohol is ignored) and not much better with various other solvent polarity parameters such as Dimroth and Reichardt's  $E_{\text{T}}(30)$  parameters<sup>29</sup> which reflect the effects of local ordering of solvent molecules in the cybotactic region around a polar solute (see Fig. 2B, the least squares lines yields  $r^2 = 0.57$ , or 0.79 if the point for *tert*-butyl alcohol is ignored). The most deviant behavior is observed in *tert*-butyl alcohol. In this solvent,  $k_6$  is smaller than in isooctane or  $\text{CCl}_4$  but is larger than would be predicted from *tert*-butyl alcohol's  $\beta_2^{\text{H}}$  or  $E_{\text{T}}(30)$  values. We have encountered similar anomalous KSEs in *tert*-butyl alcohol (*i.e.*, larger rates than would be predicted from this solvent's  $\beta_2^{\text{H}}$  value) in a number of other H-atom abstraction reactions.<sup>22,30,31</sup> We still have no explanation for this rate "enhancement" and note that it is not a general property of alcohols but appears to be confined to the more sterically demanding alcohols, particularly *tert*-butyl alcohol.<sup>30</sup>

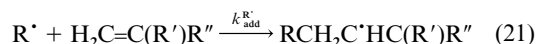
Our data indicate that  $\text{Et}_3\text{N} \rightarrow \text{BH}_2^{\cdot}$  and  $\text{BH}_3^{\cdot-}$  have rather similar reactivities in halogen atom abstraction reactions, though the latter may be slightly more reactive than the former towards some of the less reactive halides (as previously suggested for Br abstraction from *n*-PrBr).<sup>3</sup> Roberts and co-workers have reported that the relative rate of halogen atom abstraction from the  $\text{Me}_3\text{CBr}/n\text{-PrBr}$  pair by  $\text{Et}_3\text{N} \rightarrow \text{BH}_2^{\cdot}$  is  $1.2 \pm 0.1$  at 246 K<sup>4</sup> (*cf.*, a 1.7, ratio at *ca.* 298 K from Table 2) and for the  $\text{Me}_3\text{CCl}/n\text{-PrCl}$  pair by  $\text{Me}_3\text{N} \rightarrow \text{BH}_2^{\cdot}$  is 5.0 at 261 K<sup>5</sup> (*cf.*, a ratio of *ca.* 2.6, Table 2). Roberts' two rate ratios and our own two are in gratifying agreement considering the differences in temperature and the different experimental procedures by which they were obtained (EPR,<sup>4,5</sup> LFP and <sup>11</sup>B NMR). Table 2 also shows comparison of the absolute rate constants for halogen atom abstraction from alkyl halides by the two boron-centered radicals with similar data for silicon-, germanium- and tin-centered radicals. In 1986, Green and Roberts stated:<sup>13</sup> "It seems likely that the absolute reactivities of the amine-boryls towards alkyl halides are broadly similar to those of trialkylsilyl radicals." This suggestion is now confirmed, see Table 2. However, at the low temperatures used in the EPR experiments it was also found<sup>7</sup> that: " $\text{Me}_3\text{N} \rightarrow \text{B}^{\cdot}\text{HBu}$ " abstracts chlorine much more rapidly from 1-chlorobutane than does  $\text{Et}_3\text{Si}^{\cdot}$  . . . despite being . . . more *selective* than  $\text{Et}_3\text{Si}^{\cdot}$  in competitive abstraction of chlorine from"<sup>15</sup> *n*-BuCl and  $(\text{MeO})_n\text{CH}_3\text{-}_n\text{CH}_2\text{Cl}$ .<sup>15</sup> The rate enhancing effect of the  $\beta$ -oxygen at 200 K on chlorine abstraction by  $\text{Me}_3\text{N} \rightarrow \text{B}^{\cdot}\text{HBu}$  (factor of 30–45 for  $n = 3/n = 0$ ) and  $\text{Et}_3\text{N} \rightarrow \text{BH}_2^{\cdot}$  (factor of 17 for  $n = 3/n = 0$ ) is not reflected by  $\text{Et}_3\text{Si}^{\cdot}$  (factor of only 2.3–2.4 for  $n = 3/n = 0$ ).<sup>15</sup> This indicates



**Fig. 2**  $\log(k_{\text{Et}_3\text{N} \rightarrow \text{BH}_3/\text{CumO}}^{\text{S}}/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1})$  vs. A)  $\beta_2^{\text{H}}$  and B)  $E_{\text{T}}(30)$ /kcal mol<sup>-1</sup>. The numbers beside the points correspond to the solvents indicated in Table 1. The circles correspond to LFP measured rate constants and the triangle to the rate constant measured in pyridine (11) by product analysis. The solid lines are the least squares lines through all the points and the dashed lines through all the points except *tert*-butyl alcohol (4), see text.

the importance of polar effects in lowering the activation energy for halogen atom abstraction by stabilizing the transition state *via* canonical structures such as  $[(\text{RCH}_2^{\cdot} \text{Cl}^- \text{X}^+) \leftrightarrow (\text{RCH}_2^- \text{Cl}^+ \text{X})]^{\ddagger}$ .

In the absence of steric effects, the nucleophilic  $\text{Et}_3\text{N} \rightarrow \text{BH}_2^{\cdot}$  radical is expected to add more rapidly to those olefins which are more electron-deficient. Such behavior has been observed previously for addition of the nucleophilic benzyl,<sup>32,33</sup> hydroxymethyl,<sup>34</sup> *tert*-butyl<sup>35</sup> and 2-hydroxypropan-2-yl<sup>36</sup> radicals to various mono- and 1,1-disubstituted olefins.‡ Indeed, for each of these carbon-centered radicals there is a linear correlation between  $\log(k_{\text{add}}^{\text{R}}/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1})$  [eqn. (22)] and the electron affinity of the olefins [reaction (21)]:



$$\log(k_{\text{add}}^{\text{R}}/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}) = a + b(\text{EA}/\text{eV}) \quad (22)$$

Values of  $a$  and  $b$  for the four nucleophilic carbon-centered radicals are given in Table 5. It can be seen that as the radical becomes more nucleophilic both  $a$  and  $b$  increase. This is to be expected *when polar factors dominate reactivity*,<sup>32–36</sup> *i.e.*, when the activation energies are significantly lowered because the transition state is stabilized by its strong polar character. We have found that there is, in fact, a remarkably good linear correlation between  $a$  and  $b$  for these four radicals (plotted as filled circles in the inset in Fig. 3).

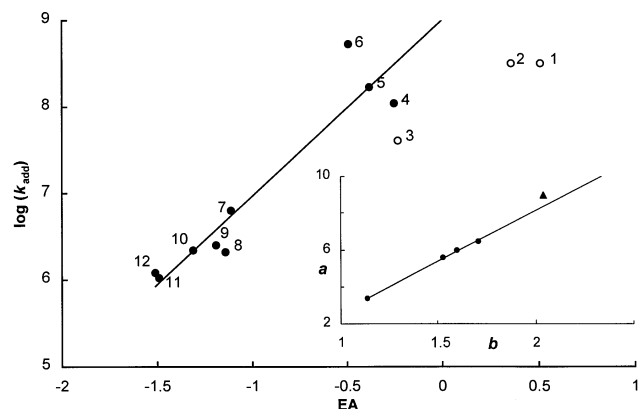
Mono-substituted and 1,1-disubstituted olefins, which would be expected to undergo exclusive, or almost exclusive, addition with  $\text{Et}_3\text{N} \rightarrow \text{BH}_2^{\cdot}$ , were chosen and rate constants for

‡ Electrophilic perfluoroalkyl radicals add more rapidly to olefins as the olefin becomes more electron rich and linear correlations are obtained when  $\log k$  values are plotted against the ionization potential of the olefins.<sup>37</sup>

**Table 5** Dimensionless parameters which describe, *via* eqn. (22), the kinetics of addition of nucleophilic radicals to mono- and 1,1-disubstituted olefins in terms of the olefins' electron affinities

Radical	<i>a</i>	<i>b</i>	Reference
PhCH <sub>2</sub> ·	3.36	1.14	32, 33
HOCH <sub>2</sub> ·	5.57	1.53	34
Me <sub>3</sub> C·	6.0	1.6	35
HOC·Me <sub>2</sub>	6.46	1.71	36
Et <sub>3</sub> N→BH <sub>2</sub> ·	9.0	2.0	This work
(CH <sub>3</sub> ) <sub>3</sub> ·	5.78	0.97	38) <sup>a</sup>

<sup>a</sup> The *a* and *b* values for CH<sub>3</sub>· do not lie on the line shown in the inset of Fig. 3 for the other five radicals. We attributed the "anomalous" behaviour of the methyl radical to its low nucleophilicity combined with its very high reactivity.



**Fig. 3** Log ( $k_{\text{add}}^{\text{Et}_3\text{N}\rightarrow\text{BH}_2\cdot}/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ) vs. EA/eV. The numbers beside the points correspond to the olefins indicated in Table 3. The least squares line is drawn through the filled circles only. The open circles have been excluded for the reasons given in the text. Inset: the correlation between *a* and *b* [see eqn. (22) and Table 5].

these addition reactions were determined. The plot of log ( $k_{\text{add}}^{\text{Et}_3\text{N}\rightarrow\text{BH}_2\cdot}$ ) vs. the EA of the olefin is shown in Fig. 3. There is, as usual,<sup>32–36</sup> a lot of scatter in this plot. However, it is clear that Et<sub>3</sub>N→BH<sub>2</sub>· is so strongly nucleophilic that it reacts at, or close to, the diffusion-controlled rate with olefins having EA ≥ −0.5 eV (*i.e.*,  $k_{\text{add}}^{\text{Et}_3\text{N}\rightarrow\text{BH}_2\cdot} = 10^8\text{--}10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ) except for  $\alpha$ -methylstyrene. The lower than "expected" rate constant for addition of Et<sub>3</sub>N→BH<sub>2</sub>· to  $\alpha$ -methylstyrene (3), and also to 1,1-diphenylethylene (2) and pentafluorostyrene (1), can probably be attributed to the fact that the double bond is twisted out of the phenyl ring plane in these olefins.<sup>39</sup> Only when the olefin's EA drops to below −1.0 eV does  $k_{\text{add}}$  drop below  $10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . The decline in  $k_{\text{add}}^{\text{Et}_3\text{N}\rightarrow\text{BH}_2\cdot}$  as the olefins' EAs decrease from −0.5 to −1.5 eV is about two orders of magnitude and this rate of decline in  $k_{\text{add}}^{\text{Et}_3\text{N}\rightarrow\text{BH}_2\cdot}$  appears to be maintained below −1.5 eV (*cf.* olefins 13 to 16). If we ignore the data points (open circles in Fig. 3) for C<sub>6</sub>F<sub>5</sub>CH=CH<sub>2</sub> (1), (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>C=CH<sub>2</sub> (2) and C<sub>6</sub>H<sub>5</sub>CMe=CH<sub>2</sub> (3) for the "twisted" geometric reason outlined above, plus, for olefins 1 and 2, because their  $k_{\text{add}}^{\text{Et}_3\text{N}\rightarrow\text{BH}_2\cdot}$  values are likely to be limited by diffusion rather than by their EAs, then the best straight line through the points (filled circles) for olefins 4–12 yields, according to eqn. (22), *a* = 9.0 and *b* = 2.0. This point is shown in the inset in Fig. 3 as a filled triangle. It lies close to the line defined by the correlation we have found for four nucleophilic carbon-centered radicals studied by Fischer and co-workers.<sup>32–36</sup> This demonstrates that Et<sub>3</sub>N→BH<sub>2</sub>· is much more nucleophilic than all four of these carbon-centered radicals.

Our limited kinetic data for hydrogen abstraction from electron deficient C–H groups by Et<sub>3</sub>N→BH<sub>2</sub>· are consistent with relative rates measured by the EPR method for the "somewhat sterically crowded"<sup>7</sup> Me<sub>3</sub>N→B'HCMe<sub>2</sub>CHMe<sub>2</sub> radical at a much lower temperature<sup>6</sup> (see last two columns of Table 4).

This is rather surprising because the ratio of the rates of H-atom abstraction from H<sub>2</sub>C(CO<sub>2</sub>Et)<sub>2</sub>/HC(CH<sub>3</sub>)(CO<sub>2</sub>Et)<sub>2</sub> pair are largest (~20) for Me<sub>3</sub>N→B'HCMe<sub>2</sub>CHMe<sub>2</sub> and decline as steric crowding about the radical center is reduced to a low of ~0.9 for Me<sub>3</sub>N→B'HBu<sup>n</sup> (Et<sub>3</sub>N→BH<sub>2</sub>· was not examined).<sup>12</sup> Therefore, it is doubtful whether our absolute Et<sub>3</sub>N→BH<sub>2</sub>· kinetic data should be combined with the Me<sub>3</sub>N→B'HCMe<sub>2</sub>CHMe<sub>2</sub> relative rates to derive even rough absolute rate constants for hydrogen atom abstraction from the less reactive substrates, such as (CH<sub>2</sub>CO<sub>2</sub>Et)<sub>2</sub>.

## Experimental

### Materials

Di-*tert*-butyl peroxide (Aldrich) was passed through a column of basic alumina prior to use. Dicumyl peroxide (Aldrich) was recrystallized from methanol. All other reagents and solvents were of the highest purity available and were further purified by standard methods only when deemed necessary.

### Laser flash photolysis (LFP)

The equipment and experimental procedures have been thoroughly described in earlier papers from this laboratory.<sup>40</sup> *tert*-Butoxyl and cumyloxyl radicals were generated by 308 nm LFP of solutions which generally contained 0.22 M di-*tert*-butyl peroxide or 0.13 M dicumyl peroxide, respectively. (These concentrations give an absorbance ~0.3 at the laser wavelength in the 7 × 7 mm<sup>2</sup> Suprasil quartz cell). All solutions of peroxide, borane (Et<sub>3</sub>N→BH<sub>3</sub> or *n*-Bu<sub>4</sub>N<sup>+</sup> BH<sub>4</sub><sup>−</sup>) and, when required, an added reagent at a known concentration were deoxygenated by purging with nitrogen for >5 min prior to LFP. Pseudo-first-order rate constants ( $k_{\text{exptl}}$ ) were determined at 298 ± 2 K using digitally averaged decay or growth curves (from up to 10 laser flashes) with monitoring at 485 nm (cumyloxyl decay), at 475 or 450 nm (BH<sub>3</sub><sup>−</sup> growth or decay), at 375 nm (Et<sub>3</sub>N→BH<sub>2</sub>· growth or decay), or at 321 nm (benzylic radicals growth). Absolute second-order rate constants were calculated by least squares fitting of plots of  $k_{\text{exptl}}$  vs. [substrate] for at least five different substrate concentrations.

### Cumyloxyl radical reaction with Et<sub>3</sub>N→BH<sub>3</sub> in pyridine by product analysis

Dicumyl hyponitrite, synthesized by a literature procedure,<sup>41</sup> was decomposed at 298 K in the dark for 10 days (15 half-lives) in nitrogen-purged pyridine in sealed Pyrex vessels containing seven different concentrations of either Et<sub>3</sub>N→BH<sub>3</sub> or cyclohexane. Relative and absolute yields of cumyl alcohol and acetophenone were then determined by GC/FID on a Hewlett Packard 5890 instrument using a 25 m × 0.02 mm (id) HP-Ultra-2 column and 1,4-dichlorobenzene as the internal standard.

There was a concern that when the triethylamine–borane complex was dissolved in pyridine ligand exchange might be fast on the time scale of our experiments ( $t_{1/2} = 16 \text{ h}$ ). The kinetics of exchange were examined *via* <sup>11</sup>B NMR (128.4 MHz, Bruker DRX400) by monitoring the decay of the Et<sub>3</sub>N→BH<sub>3</sub> peak (13.5 ppm) and the grow-in of the C<sub>3</sub>H<sub>5</sub>N→BH<sub>3</sub> peak (12.1 ppm) against a reference standard (Et<sub>2</sub>O·BF<sub>3</sub>). At a concentration comparable to those used in our cumyloxyl radical experiments, pseudo-first-order conditions apply and time (*t*) was plotted against ln([Et<sub>3</sub>N→BH<sub>3</sub>]<sub>*t*</sub>/[Et<sub>3</sub>N→BH<sub>3</sub>]<sub>0</sub>). The plot gave a straight line ( $r^2 = 0.88$ ) and its slope gave a rate constant of  $3.9 \times 10^{-6} \text{ s}^{-1}$  corresponding to  $t_{1/2} = 50 \text{ h}$ .

### Competitive kinetics of halide abstraction by Et<sub>3</sub>N→BH<sub>2</sub>·

*tert*-Butoxyl radicals were generated by thermal decomposition of di-*tert*-butyl hyponitrite (298 K, in the dark, 10 days) in nitrogen-purged benzene containing Et<sub>3</sub>N→BH<sub>3</sub>, *n*-PrBr and

**Table 6** Comparison of calculated (B3LYP/6-311+G(2d, 2p)//AM1) and experimental electron affinities for some C<sub>6</sub>H<sub>5</sub>X and C<sub>6</sub>F<sub>5</sub>X compounds

Substrate	Calcd. EA/eV	Expt. EA/eV <sup>a</sup>
C <sub>6</sub> H <sub>5</sub> O <sup>•</sup>	2.20	2.25
C <sub>6</sub> F <sub>5</sub> O <sup>•</sup>	3.19	3.34
C <sub>6</sub> H <sub>5</sub> <sup>•</sup>	1.01	1.01
C <sub>6</sub> F <sub>5</sub> <sup>•</sup>	2.59	2.7
C <sub>6</sub> H <sub>5</sub> CN	0.25	0.26
C <sub>6</sub> F <sub>5</sub> CN	1.05	1.08
C <sub>6</sub> H <sub>5</sub> COCH <sub>3</sub>	0.35	0.33
C <sub>6</sub> F <sub>5</sub> COCH <sub>3</sub>	0.96	0.88
C <sub>6</sub> H <sub>5</sub> CH=CH <sub>2</sub>	-0.20	-0.25 <sup>b</sup>
C <sub>6</sub> F <sub>5</sub> CH=CH <sub>2</sub>	0.51	<sup>c</sup>

<sup>a</sup>From ref. 45 unless otherwise noted. <sup>b</sup>Ref. 46. <sup>c</sup>Not available.

an alkyl chloride. The concentration of the hyponitrite was 0.5 mM, *i.e.*, *ca.* 4% that of the Et<sub>3</sub>N→BH<sub>3</sub>; the concentration of which was 12 mM. Thus, since almost two *tert*-butoxyl radicals are generated from each molecule of hyponitrite, only *ca.* 8% of the amine–borane was consumed. The concentration of *n*-PrBr was 10 mM and the concentrations of the alkyl chlorides were adjusted so that the yields of Et<sub>3</sub>N→BH<sub>2</sub>Br and Et<sub>3</sub>N→BH<sub>2</sub>Cl were very roughly equal ([RCI] varied from 0.5 to 5 M). The relative yields of these two products were measured by <sup>11</sup>B NMR: BCl (−5.5 ppm) and BBr (−8.0 ppm) both relative to (added) Et<sub>2</sub>O·BF<sub>3</sub>.

### Theoretical calculations

The geometry was first optimized using the AM1<sup>42</sup> semi-empirical method for both the dipole moment and the electron affinity calculations. The AM1 geometries were then used to calculate the dipole moment and the single point energies were computed using the B3LYP functional<sup>43,44</sup> with the 6-311+G(2d, 2p) basis set.

The electronic energies and zero-point energies were summed to give *E*<sub>0</sub>, the total energy at 0 K. The electron affinities were calculated as *E*<sub>0</sub> (anion) − *E*<sub>0</sub> (parent). The validity of the calculated EA values for C<sub>6</sub>F<sub>5</sub>CH=CH<sub>2</sub> was checked by calculations on various C<sub>6</sub>H<sub>5</sub>X and C<sub>6</sub>F<sub>5</sub>X compounds for which experimental EA values were also available<sup>45</sup> (see Table 6). All calculations were performed using the Gaussian 98 package.<sup>28</sup>

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