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

by

Brad Sheeller

**A thesis submitted to
the Faculty of Graduate Studies and Research
in partial fulfilment of
the requirements for the degree of
Masters of Science**

**Department of Chemistry
Carleton University
Ottawa, Ontario**

Date Defended: 31 July, 2001

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**“Absolute rate constants for some reactions
of the triethylamine-boryl radical
and the borane radical anion”**

**submitted by Brad Sheeller
in partial fulfillment of the requirements for
the degree of Masters of Science**

Chair of Chemistry Department

Thesis Supervisor

Abstract

Laser flash photolysis (LFP) of di-*tert*-butyl peroxide or dicumyl peroxide at ambient temperatures in the presence of $\text{Et}_3\text{N} \rightarrow \text{BH}_3$ and BH_4^- generated the title radicals which were found to have broad, featureless absorptions in the visible region. Rate constants for the H-atom abstraction from $\text{Et}_3\text{N} \rightarrow \text{BH}_3$ by cumyloxyl radicals show a small solvent dependence, eg., 12×10^7 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 $\text{Et}_3\text{N} \rightarrow \text{BH}_2^\bullet$ and $\text{BH}_3^{\bullet-}$ from a number of chlorides and bromides were determined by LFP and by competitive kinetics. Rates of addition of $\text{Et}_3\text{N} \rightarrow \text{BH}_2^\bullet$ to 1- and 1,1-substituted olefins increase dramatically as the electron affinity of the olefin increases, confirming the nucleophilic character of amine $\rightarrow$ boryl radicals. A comparison of the present results with literature data for the addition to olefins of four nucleophilic carbon-centred radicals proves that $\text{Et}_3\text{N} \rightarrow \text{BH}_2^\bullet$ 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 $\text{Et}_3\text{N} \rightarrow \text{BH}_2^\bullet$ are also reported.

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List of Abbreviations

Ac – Acetyl

EA – Electron Affinity

ESR – Electron Spin Resonance

Et – Ethyl

HBA – Hydrogen Bond Acceptor

HBD – Hydrogen Bond Donor

KSE – Kinetic Solvent Effect

LFP – Laser Flash Photolysis

Me – Methyl

OD – Optical Density

Ph – Phenyl

PRC – Polarity Reversal Catalysis

Pyr – Pyridine

1 Introduction

The main purpose of this research was to measure the absolute rate constants for a variety of reactions undergone by two boron-centred radicals with the hope that these data will eventually prove useful to synthetic organic chemists. Ever since Gomberg's discovery of the triphenylmethyl radical, the formation, structures and reactions of carbon-centred free radicals have been extensively studied. Although the triethylamine→borane complex, $\text{Et}_3\text{N} \rightarrow \text{BH}_3$, is isoelectronic with its alkane counterpart, $\text{Et}_3\text{C}-\text{CH}_3$, and the triethylamine→boryl radical, $\text{Et}_3\text{N} \rightarrow \text{BH}_2^\bullet$, is isoelectronic with the alkyl radical, $\text{Et}_3\text{C}-\text{CH}_2^\bullet$, very little is known about boron-centred radicals. Boron radicals have some unique properties that could and should be exploited in synthesis. With the rate constants provided herein, a good organic chemist should be able to plan rational, boron-centred radical based syntheses of complex molecules. This ability to plan provides the organic chemists with an assured successful outcome and optimized yields by correctly choosing the reagents and their concentrations just as is done today for syntheses based on tin-centred radicals¹.

1.1 Current Knowledge on the Reactivity and Chemistry of Amine→Boryl Radicals and the Borane Radical Anion

In a major series of publications that began almost 20 years ago, Roberts and co-workers have reported the structure and elementary reactions of amine→boryl radicals, e.g., $\text{Et}_3\text{N} \rightarrow \text{BH}_2^\bullet$ ^{2,3} and the borane radical anion, $\text{BH}_3^{\bullet-}$,^{4,5}. ESR spectroscopy was used

to show that these radicals exhibit some fascinatingly “different” homolytic chemistry from that of more familiar radicals such as alkoxyls, $\text{RO}^\bullet$, and trialkyltins, $\text{R}_3\text{Sn}^\bullet$. As opposed to most of the “familiar” radicals, amine→boryl radicals are strongly nucleophilic. Furthermore, the influence of polar factors on the reaction of uncharged free radicals has been recognized for over fifty years⁶ and it is well established that polar factors play an important role in determining the chemo- and regio-selectivities of hydrogen atom abstraction reactions.⁶⁻⁹ Favourable thermodynamics and favourable polar effects, allow *tert*-butoxyl radicals to readily abstract hydrogen from electron-rich C-H groups such as those attached to oxygen in an alcohol or an ether, whereas H-atom abstraction from electron-deficient C-H groups such as those in acetonitrile¹⁰ and from those α to carbonyl substituents (in esters, lactones and related compounds)^{11,12} are very slow because of unfavourable polar effects despite equally favourable thermodynamics. For example, although reactions (1) and (2) are both exothermic¹³⁻¹⁵ by *ca.* 50 kJ mol⁻¹, the former proceeds much more rapidly than the latter:

Although electron-deficient C-H groups do not easily donate hydrogen atoms to electrophilic alkoxyl radicals, this is not the case for amine→boranes which react readily with alkoxyl radicals to yield amine→boryl radicals. Moreover, the nucleophilic, electron-rich amine→boryl radicals can, in turn, readily abstract hydrogen from electron-deficient C-H groups because of the favourable polar effects. These traits have been

exploited and developed by Roberts. For example¹⁰, the cyanomethyl radical can be generated from acetonitrile by the following two reactions:

This two-step method of H-atom abstraction from electron-deficient C-H groups has been christened “polarity reversal catalysis” (PRC) by Roberts^{10-12,16}.

Reactions 3 and 4 are a catalytic process for the otherwise very slow reaction:

PRC has been further developed into synthetically useful chain reactions (with chains being carried by amine→boryl and *tert*-butoxyl radicals)^{16,17} as illustrated in the following example involving the reaction of methyl acetate with *tert*-butyl-1,1-dimethylallyl peroxide:

With chiral amine→boryl radicals in which the *B*-alkyl group is chiral, an enantioselective hydrogen atom abstraction may occur from a C-H group which is α to a ketone or a carboxylic acid derivative¹⁸⁻²⁰, as shown in reaction 6.

Although many stereoselective radical reactions are now known, fewer enantioselective homolytic processes have been identified and enantioselective atom transfer reactions are particularly uncommon¹⁸. However, Roberts and coworkers found some chiral amine→boryl radicals to have enantioselectivity constants, s^* , as high as 21.¹³

Amine→boryl radicals and the borane radical anion can also abstract halogen atoms from alkyl halides,^{2,3,5,10,12,21-23} add to olefins, aromatics and other unsaturated compounds,^{3,5,10,20,24} and generally do chemistry reminiscent of silicon- and tin-centered radicals, 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.¹ 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 ambient temperatures which could prove useful to synthetic chemists. To remedy this deficiency, I have applied the technique of laser flash photolysis (LFP) to determine absolute rate constants for the formation (via alkoxyl radicals) and some reactions of the $\text{Et}_3\text{N} \rightarrow \text{BH}_2^\bullet$ and $\text{BH}_3^{\bullet-}$ radicals at ambient temperatures.

* The enantioselectivity constant, s , is equal to k_A/k_B , where k_A and k_B are the rate constants for abstraction from the more and from the less reactive enantiomers, respectively.²⁰

1.2 Laser Flash Photolysis and the Formation of Radicals

The use of free radicals in organic synthesis¹ has grown enormously over the past 10-15 years as chemists have learned to take advantage of some of their unique properties such as their generally high reactivity and, generally, small solvent effects on rates and products. Moreover, there is usually no requirement for protection/deprotection strategies.

The most generally useful method for measuring the absolute rate constant for a free radical reaction is to generate a 'pulse' of the radical in question within a short interval of time and then monitoring the decay of this radical, or growth of a product radical, in real time. Today the most favoured method for generating the radical pulse is to use a pulse of light²⁵. This technique is called "flash photolysis" and was introduced by Porter in 1949²⁸. The advent of high powered ultra-violet lasers in the 1970's simplified and revolutionized the technique, which is now known simply as LFP, standing for laser flash photolysis. The laser allows the generation of a short intense pulse of light. Absorption of a quantum of laser light by a *suitable* molecular precursor will lead to the formation of two free radicals. These radicals are formed from the photoexcited molecular precursor either by a direct dissociation from the excited singlet state, e.g. peroxides, as shown in reaction 7, or after intersystem crossing to the triplet manifold (as happens in the Norrish Type I photochemistry of ketones), shown in reaction 8.

In some cases, a triplet biradical may be formed via an intramolecular reaction of the excited triplet state (as happens in the Norrish Type II photochemistry of ketones):

In the present work, the laser was used to generate the alkoxy radicals through the direct dissociation of the parent dialkyl peroxides and then the transient radicals were monitored by time-resolved UV spectrophotometry. The detector was set to monitor a single wavelength as a function of time. The chosen wavelength is one at which the relevant transient species shows a characteristic absorption, ideally a wavelength that is exclusive to that species. The actual monitoring wavelength was chosen after examining the complete spectrum of the transient radicals produced in the laser pulse.

1.3 Apparatus

The components used for a typical laser flash photolysis experiment are shown in Figure 1. They include: the sample cell, excitation source (the laser), monitoring source (the UV-Vis. lamp), optical lenses and filters, detectors, and analysis/output devices (digitizer/computer).²⁷

Sample Cell

The sample cells used were 7 x 7 mm Suprasil quartz tubes.

Laser Excitation Source

One of the most important aspects of any LFP experiment is the selection of the appropriate laser. The laser used in the experiments described in this thesis was a Lumonics Excimer 500. The laser was charged with a gas mixture of 40 Torr Xenon, 3100 Torr of Neon, and 50 Torr of a gas mixture made up of 5 % HCl, 1 % H₂ and 94 % Neon, which provided an excitation wavelength of 308 nm.

The output of the laser was generally 35-70 mJ and neutral density filters were used to attenuate the output in order to avoid high radical concentrations which would decay by radical/radical reactions with second-order kinetics. The pulse width (pulse duration) of the laser was approximately 10 ns.

Monitoring Source

A xenon arc lamp with an output of ~75 W was used for monitoring. This lamp was operated in a pulse mode; i.e., the intensity was increased by a factor of 20-100 during the essential few milliseconds. The light which was focused to a beam with ~1 mm radius where it passed through the sample.

Detector

The detector for the laser flash experiments consisted of a monochromator / photomultiplier tube (MC/PMT) combination. The monochromator was located in front of the PMT and when a photon of the selected wavelength struck the cathode of the PMT, an electron was emitted. The PMT was wired as a six-dynode chain for fast response and to prevent saturation at high intensities.

Figure 1. Schematic diagram of laser flash photolysis apparatus with UV-Vis detection.

Data Gathering

Transient digitizers are used to convert the PMT output into digital form and transfer the data to a computer for further processing. The digitizer was a Tektronix, model 7912AD programmable digitizer.

Data Processing

The results produced in an LFP experiment are the intensity of the monitoring beam at an array of data points (exactly 100) in the form of the PMT voltage as a function of time. The data points are converted into changes in optical densities via the equation below.

$$A_t = \Delta OD = -\log(1 - \text{signal} / IO) = -\log(I_t / IO)$$

where IO is the intensity of the monitoring beam measured as a voltage, and signal is the signal voltage as a function of time. I_t is equal to $IO - \text{signal}$. The signal created was captured by a Tektronix 2440 digital storage oscilloscope which was interfaced to a 386 SX personal computer. The program used to analyze the data was written in FORTRAN.

Corrections to the Data

To improve the quality of data, two different types of corrections may be required, namely 'baseline' and 'fluorescence' corrections.

Some unwanted phenomena, such as *bleaching* (a decrease in optical density caused by absorbing molecules) or noise due to the electronics of the laser and the lamp, in addition to the baseline drift, may be reduced by making a baseline correction. The baseline correction is achieved by subtracting a signal containing only the monitoring

beam (laser blocked) from one containing the transient (laser on) together with the monitoring beam. This method was used for time domains up to a microsecond.

Species in the sample that fluoresce will contribute to decreases in the apparent absorption. To correct for this, the signal is recorded with the monitoring beam on and off while the laser is firing. This correction must also be made when the time domain is approaching the laser pulse width.

Samples

Samples were prepared at a concentration such that the OD at 308 nm was ~0.3 in the 7 x 7 mm Supracil quartz cell. Samples were flashed no more than 10 times and the signals from these 10, or fewer, flashes were averaged. Fresh samples were prepared for each kinetic measurement and purged with N₂ as described in the experimental section.

1.4 Selected Radical Reactions

There are two main ways in which radicals can react with each other, *combination* and *disproportionation*. Combination reactions involve two radicals combining their unpaired electrons to form a new σ bond, as shown below. When these radicals are both the same, this process is called dimerization.

Disproportionation, on the other hand, happens when two radicals react and transfer an atom, usually hydrogen, to give saturated and unsaturated molecular products, as is shown in the disproportionation of two ethyl radicals:

There are several types of radical/molecule reactions. One of the most common is hydrogen abstraction^{28,29}:

The factors governing the rate of intermolecular abstraction of hydrogen by a radical, $\text{B}^\bullet$, from a molecule, A-H are³⁰: i) the strength of the bond which is formed, B-H ; ii) the strength of the bond which is broken, A-H ; iii) the triplet repulsion between $\text{A}^\bullet$ and $\text{B}^\bullet$ since the three electrons involved in the reaction will orient their spins in the transition state as shown below.

Other common reactions that a radical may undergo include its addition to an unsaturated molecule, fragmentation, cyclization (and ring opening), atom abstraction (other than hydrogen) and migration. Migration is the transport of an atom or group from one position in the radical to another, resulting in a different and thermodynamically more stable radical.

1.5 Hydrogen Abstraction from $\text{Et}_3\text{N} \rightarrow \text{BH}_3$ and BH_4^- by *tert*-Alkoxyl Radicals

Giles and Roberts⁴ first showed that the borane radical anion may be generated readily by hydrogen abstraction from BH_4^- by alkoxyl radicals. This publication was soon followed by a communication² reporting that amine adducts of boryl radicals could be generated in a similar way from amine-borane complexes:

There is very extensive literature regarding the absolute rate constants for the reactions of alkoxyl radicals with organic substrates in the liquid phase³¹. The alkoxyl radicals most commonly used to react with the organic substrates are *tert*-butoxyl and cumyloxyl radicals. Most of these kinetic data have been obtained using *tert*-butoxyl and cumyloxyl radicals generated “instantaneously” by 308 nm laser flash photolysis of their parent peroxides:

However, in a few experiments the *tert*-butoxyl and cumyloxyl radicals were generated thermally from their parent hyponitrites.

The reaction of the generated alkoxyl radicals with amine→boranes, to produce the corresponding amine→boryl radical, is believed to be fast^{2-5,10-12,16-24}, but no directly measured absolute kinetic data are available. An indirect competitive kinetic procedure³² has yielded rate constants for hydrogen abstraction from Et₃N→BH₃ by *tert*-butoxyl radicals in *tert*-butyl benzene ($2.6 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$) and pyridine ($1.3 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$). However, these results do not completely agree with our own direct measurements (see Results, Section 3.3).

1.6 Reactions of Et₃N→BH₂[•] and BH₃^{•-}

1.6.1 Halogen atom abstraction by Et₃N→BH₂[•] and BH₃^{•-}

In addition to demonstrating the generation of BH₃^{•-} by ESR, Giles and Roberts⁴ also showed that this radical could rapidly extract halogen atoms from *n*-propyl halides (Cl, Br, I). Later Roberts and co-workers showed, again by ESR spectroscopy at low temperatures, that the triethylamine→boryl radical, as well as the borane radical anion, will abstract halogen atoms from many different organic halides^{2,3,5,10,12,21-23}:

Some of the aforementioned studies include measurements of a few relative rates of reaction of different halides and there is one study that reports a few relative rates halogen atom abstraction from β-alkoxyl alkyl chlorides²³. However, absolute rate

constants are absolutely required if these reactions are ever to prove to be synthetically useful, or at least, this certainly was the case for halogen atom abstractions by tri-*n*-butyltin radicals (one of the fixtures of modern synthetic organic chemistry)¹.

1.6.2 Addition Reactions of $\text{Et}_3\text{N}\rightarrow\text{BH}_2^\bullet$

In their initial publication, Giles and Roberts even showed that $\text{BH}_3^{\bullet-}$ could add to azides⁴ and later, to a few alkenes and arenes⁵. Later, the nucleophilic triethylamine $\rightarrow$ boryl radical was also shown by ESR spectroscopy at low temperatures to be able to add to many types of olefins, aromatics and other unsaturated compounds,^{3,10,21,24} as shown in the following addition to propyne:

Examining the absolute kinetics of these reactions should throw considerable light on the nucleophilicity of the triethylamine $\rightarrow$ boryl radical.

1.6.3 Hydrogen Atom Abstraction by $\text{Et}_3\text{N}\rightarrow\text{BH}_2^\bullet$

Roberts and coworkers¹¹ have described how amine $\rightarrow$ borane complexes can act as 'donor' polarity reversal catalysts for hydrogen atom abstractions from electron-deficient C-H bonds by electrophilic alkoxyl radicals. The basis of *polarity reversal catalysis* (PRC) is to replace a single-step abstraction (reaction 9), which is slow because of unfavourable polar effects in the reactants ($\text{RO}^\bullet$ and H-EI are both electron-deficient species), with a two-step process (reactions 10 and 11) in which the radicals and

substrates are polarity matched¹⁶ (an electron-deficient species with an electron-sufficient species) and benefit from the favourable charge transfer interactions in the transition state¹⁸.

where $\text{EI}^\bullet$ and $\text{Nuc}^\bullet$ are the electrophilic and nucleophilic radicals, respectively.

The electrophilic alkoxyl radical preferentially abstracts hydrogen from the electron-rich BH_3 group³ of the amine→borane complex, a reaction which can be followed by a rapid hydrogen abstraction from an electron deficient C-H by the amine→boryl radical. This two step reaction, in which the amine→borane complex functions as a catalyst (reactions 12 and 13) is much faster than the corresponding abstraction from an electrophilic compound by alkoxyl radicals (reaction 9).

Roberts and coworkers have shown that amine→boranes efficiently catalyze hydrogen abstraction by alkoxyl radicals from the α -CH group of esters^{10,11}, nitriles^{10,11}, ketones¹⁰ and cyclopentadiene³³.

Some amine-borane complexes can even show interesting selectivity in hydrogen atom abstraction using amine →boryl radicals which contain a chiral *B*-alkyl group^{11,18-20}, such as isopinocampheylborane, which abstracts hydrogen from the $\text{CH}_3\text{C}(\text{O})$ group of 3-

methyl-butan-2-one, $\text{CH}_3\text{COCH}(\text{CH}_3)_2$, whereas the electrophilic *tert*-butoxyl radical abstracts the tertiary hydrogen from the isopropyl group¹¹. PRC has also been found to have further synthetic applications in chain reactions (with the chains being carried by amine→boryl and *tert*-butoxyl radicals)^{16,17}.

1.6.4 β -Scission of $\text{Et}_3\text{N}\rightarrow\text{BH}_2^\bullet$

Along with halogen abstractions, addition reactions and hydrogen abstractions, the triethylamine→boryl radical may also undergo what is known as a β -scission³. In this unimolecular reaction the amine-boryl radical loses one of its ethyl groups as an ethyl radical and a new bond is formed between the nitrogen and boron atoms.

Even though there is a relatively strong primary C-N bond³ in $\text{Et}_3\text{N}\rightarrow\text{BH}_2^\bullet$, it undergoes cleavage rapidly, in comparison to its hydrocarbon isoelectronic counterpart, $\text{Et}_3\text{CCH}_2^\bullet$ ²¹.

1.7 Kinetics of Radical Reactions

The aim of radical chemical kinetics are³⁴⁻³⁶: (1) to experimentally determine the rate of a radical reaction and its dependence on parameters such as concentration, temperature, pressure, solvent, etc.; and (2) to develop an understanding of the mechanism of a radical mediated reaction, e.g., the number of steps involved and the nature of any intermediates which may be formed.

1.7.1 The Rate Equation

The interpretation of kinetic data begins with a hypothetical sequence of elementary steps, each characterized by two rate constants, one for the forward and one for the reverse reaction. From this hypothetical mechanism a rate equation is derived, predicting the dependence of the observed reaction rate on concentrations and on rate constants. In order to understand a rate law, it is important to remember that the order of a reaction is the sum of the exponents of the concentration factors in the experimental rate law and is not necessarily the same as the molecularity which refers to the number of elementary particles involved in an elementary reaction.

This hypothetical mechanism is tested against experimental observations and if the form of the rate equation meets the test of the experiment, it may be possible to derive from the data numerical values for the rate constants of the proposed elementary reaction steps. While inconsistency between hypothetical and experimental data is clear grounds for modifying or rejecting a mechanistic hypothesis, agreement does not prove the proposed mechanism is correct.

1.7.2 Rates of Reactions

Consider a reaction of the form:

where the concentration of the species are [A], [B], and [C] at some instant in time. The rate of consumption of reactant A is:

$$v_A = -\frac{1}{a} \frac{d[A]}{dt}$$

The rate of change in the concentrations of the components with respect to one another is given by:

$$\frac{1}{a} \frac{d[A]}{dt} = \frac{1}{b} \frac{d[B]}{dt} = -\frac{1}{c} \frac{d[C]}{dt}$$

It is often found that the rate of reaction is proportional to the concentration of the reactants raised to an integral power (usually 1 or 2). For example, it may be found that the rate is proportional to the concentrations of the two reactants A and B and that:

$$v = k[A][B]$$

where the coefficient k is called the *rate constant* for the reaction.

1.7.3 Unimolecular Kinetics

One of the most frequently encountered kinetic forms is that of the first-order rate equation, as shown in this reversible reaction:

The rate of disappearance of A, is given by equation 15 and the rate of disappearance of B is given by equation 16:

$$-\frac{d[A]}{dt} = k_1[A] - k_{-1}[B] \quad (15)$$

$$-\frac{d[B]}{dt} = -k_1[A] + k_{-1}[B] \quad (16)$$

Equation 15 and 16 constitute a mathematical model for the dynamics of reaction 14, and the predicted rates of change in the concentrations of A and B are given by sums of terms, each of which contain only the first power of each concentration. Therefore, the kinetics are said to be of first order. In reaction 14 we have assumed the reaction is: A changes to B and B changes to A without the intermediacy of a third species, I. That is, reaction 14 does not occur via,

Reaction 14 is therefore an elementary reaction, because there are no intermediates.

A first-order, unimolecular reaction may be simplified if $k_1 \gg k_{-1}$. Then the chemical equation can be written as:

Now the rate of disappearance of reactant A, is given by :

$$-\frac{d[A]}{dt} = k_1[A]$$

The differential equation is then easily solved, the boundaries are: at $t=0$ the concentration of reactant A is $[A]_0$, and at time t it is $[A]_t$, hence:

$$[A]_t = [A]_0 \exp(-k_1 t)$$

A similar expression is obtained in terms of product B, except that the solution will be an exponential growth.

1.7.4 Bimolecular Kinetics

Second-order kinetics arise when the sum of the powers of the reactant concentrations in the rate law is equal to two. The two most common cases involve either the same or different reactants.

Case I

An elementary reaction in which the encounter of reactant A with another molecule of reactant A may form an *activated complex* in the transition state and give product C:

The rate law is given by:

$$-\frac{d[A]}{dt} = k[A]^2$$

The solution to this equation is:

$$[A]_t = \frac{[A]_0}{1 + kt[A]_0}$$

If a reaction is second-order, a plot of $1/[A]_t$ against t should yield a straight line, and the slope of the line is equal to the rate constant; i.e.,

$$\frac{1}{[A]_t} = \frac{1}{[A]_0} + kt$$

Case II

An elementary reaction in which the encounter of two different reactants, A and B, may form an *activated complex* which is transformed into product C:

The rate law for this 'mixed-second-order' kinetics is:

$$-\frac{d[B]}{dt} = -\frac{d[A]}{dt} = k[A][B]$$

By making the appropriate substitution, $-d[A] / dt = d\{[A]_0 - x\} / dt = dx / dt$;

$$kt = \frac{1}{[A]_0 - [B]_0} \ln \left(\frac{[A]_t[B]_0}{[A]_0[B]_t} \right) \quad (18)$$

1.7.5 Pseudo-First Order Kinetics

Equation 18 can be greatly simplified if the concentration of one reactant is kept 'constant' during the reaction. The easiest way of achieving this is to have one reactant in a large excess relative to that of the other reactant so that the rate of change of the reactant in excess, over time, is essentially zero. In the bimolecular reaction 17, if reactant B is present in a large excess over reactant A it can be considered to remain constant over the course of the reaction. In this case, we can write:

$$-\frac{d[A]}{dt} = k_{\text{obs}}$$

where $k_{\text{obs}} = k[A]$.

The absolute bimolecular rate constant is obtained by measuring the rate in the presence of a large excess of B over A, then dividing k_{obs} by the concentration of A. To reduce experimental errors, it is best to measure the observed rate, k_{obs} , with at least five different concentrations of A. Then the observed rate is plotted against the concentration of A to give a straight line with a slope that is equal to the absolute bimolecular rate constant.

1.7.6 Half Lives

A useful indicator of the rate of a chemical reaction is the time it takes for the concentration of a reactant to fall to half its initial value. The half-life depends on the initial concentration of the substance in a characteristic way that depends on the order of the reaction. The equations for half-lives are obtained by solving the reaction kinetics for the case when the concentration of A decreases from $[A]_0$ to $\frac{1}{2}[A]_0$.

For a first-order reaction, the half-life is given by:

$$t_{\frac{1}{2}} = \frac{\ln 2}{k}$$

Note: for a first-order reaction, the half-life is independent of the initial concentration of A, $[A]_0$.

In the case of a second order reaction (both reactants the same) the equation for the half-life is:

$$t_{\frac{1}{2}} = \frac{1}{k[A]_0}$$

1.8 Kinetic Solvent Effects

The rates of radical reactions are commonly assumed to be independent of solvent and there is certainly no kinetic solvent effect (KSE) on hydrogen abstraction from a hydrocarbon by an alkoxyl radical³⁷. Thus, the rate constant for hydrogen atom abstraction from cyclohexane by the cumyloxyl radical has been measured in several different solvents with varying polarities, dielectric constants, hydrogen bond donor and acceptor properties, and it has been found to be essentially unchanged for all solvents examined³⁷. In sharp contrast, the hydrogen atom abstraction from phenol by alkoxyl radicals is very much dependent upon solvent^{38,39}.

1.8.1 A Model for Kinetic Solvent Effects based on Hydrogen Bonding

To rationalize the observed KSE for hydrogen atom abstraction from phenol by the cumyloxyl radical, Ingold *et al.*³⁸ have constructed a simple solvent-substrate interaction model:

where XOH is phenol and S is a solvent. The observed effects of solvents on the rate constants for these reactions can be accounted for in a roughly quantitative manner by making four basic assumptions^{38,40}:

- i) Each substrate molecule, XOH, can act as a hydrogen bond donor to a single hydrogen bond acceptor solvent, S, at any one time.

- ii) The magnitude of the equilibrium constant for the formation of each XOH-S hydrogen bonded complex is essentially independent of the nature of the surrounding medium.
- iii) Alkoxyl radicals cannot, for steric reasons, directly abstract the hydroxylic hydrogen atom from the XOH-S complex (meaning that the solvent molecule must first be removed and replaced by the attacking radical).
- iv) The hydrogen bond/non-hydrogen bond equilibrium is established rapidly in comparison to the rate of hydrogen atom abstraction.

In the above model, it is the equilibrium constant, K^S , that will be varying from solvent to solvent and will be the main or sole contributing factor to the different reaction rates in the different solvents.

1.8.2 A Model for Kinetic Solvent Effects based on Gibb's Free Energy

Ingold and coworkers recognized that the above model was an over simplification and that it would probably be better if represented by a less specific and therefore more general model. The new model⁴¹ uses the transition-state approach and is therefore based on the Gibb's free energy of activation, $\Delta G^\ddagger$.

The solvated reactant in solvent II has a lower free energy than in solvent I and the reaction will therefore be slower in solvent II, since $k \propto \exp(-\Delta G^\ddagger)$.

However, for a different reaction, the solvent could affect the free energy of the activated complex instead of (or in conjunction with) affecting the reactants.

In this system, the solvated activated complex in solvent II will react faster than in solvent I, due to the lower $\Delta G^\ddagger$ value.

1.8.3 Information on Various Empirical Solvent Parameters

In any analysis of solvent effects on chemical reactions, it is customary to seek a linear relationship between some empirical solvent parameter and the logarithm of the rate constant for a reaction, i.e., a linear free energy relationship⁴². The parameters required to fit a linear free energy relationship will describe some property of the solvents.

Abraham's Solvent Parameter, β_2^H

The majority of the parameters used to characterize solvent-solute interactions are based on enthalpy in the form of calorimetric measurements. However, M.H. Abraham has developed parameters to characterize hydrogen bonding based on Gibb's free energy. These parameters are based on the change in free energy for the one-to-one complex formed between an acid and a base. One particular parameter, β_2^H ,⁴³ uses a β -scale of solvent hydrogen bond acceptor (HBA) basicities to describe the solvent's ability to accept a hydrogen bond. The β_2^H parameter is determined from equilibrium constants measured for the following reaction:

Where A-H is the hydrogen bond donor and B is the hydrogen bond acceptor. Since the hydrogen bonding of the solvent (eg., B) to the substrate (eg., A-H) can affect the rate at which the hydrogen abstracting agent may attack the substrate, this can be used as a measure of solvent effects.

Dimroth and Reichardt's Solvent Parameter, $E_T(30)$

Many spectroscopic parameters of solvent polarity have been derived from solvent-sensitive standard compounds absorbing electromagnetic radiation in spectral ranges corresponding to UV/Vis, IR, ESR, and NMR spectra⁴². In 1958, Kosower^{44,45} set-up the first comprehensive solvent scale by defining his polarity parameter, Z, as the molar transition energy, E_T , expressed in kcal/mol, for the charge transfer absorption band of 1-ethyl-4-methoxycarbonylpyridinium iodide:

$$Z \equiv E_T = h \times c \times \tilde{\nu} \times N_A$$

where h is Planck's constant, c is the velocity of light in a vacuum, $\tilde{\nu}$ is the wave number of the photon which produces the electronic excitation, and N_A is Avogadro's number.

This method was incorporated by others who used the longest-wavelength intermolecular transition of different dyes.

Dimroth and Reichardt⁴⁶ have proposed such a solvent polarity parameter, $E_T(30)$ based on the transition energy for the longest-wavelength solvachromic absorption band of the pyridium-*N*-phenoxide betaine dye (dye no. 30 in ref. 46), as shown below:

The $E_T(30)$ values provide an excellent and very sensitive⁴² characterization of the polarity of solvents, with high $E_T(30)$ values corresponding to high solvent polarity.

2 Experimental

2.1 Materials

All solvents (benzene, iso-octane, carbon tetrachloride, *tert*-butylbenzene, *tert*-butanol, ethyl acetate, dimethyl sulfoxide, methyl acetate, methyl formate, acetonitrile, and pyridine) were of the highest purity available. Triethylamine→borane complex, benzyl bromide, *tert*-butyl bromide, cyclohexyl bromide, allyl cyanide, vinyl trimethylsilane, allyl alcohol, and allyl benzene were purified by vacuum distillation, while 3,3-dimethyl-1-butene, 2-methoxypropene, and propyl chloride were purified by an ambient distillation at 1 atmosphere. Di-*tert*-butyl peroxide was passed through a column of basic alumina prior to use. Tetrabutylammonium borohydride and dicumyl peroxide were recrystallized from methanol. All other reagents (chloroform, benzyl chloride, *tert*-butyl chloride, cyclohexyl chloride, propyl bromide, dichloromethane, 2,3,4,5,6-pentafluorostyrene, 1,1-diphenylethylene, α -methylstyrene, β -methylstyrene, vinyl acetate, isopropenyl acetate, ethyl vinyl ether, vinylidene chloride, benzonitrile, diethyl succinate, methyl acrylate, methyl methacrylate, triethyl methane tricarboxylate, diethyl malonate, ethyl acetate, diethyl methyl malonate) were of high purity (>99%) and were used as received. All compounds were purchased from Aldrich.

2.1.1 Hyponitrite Synthesis

Neither di-*tert*-butyl hyponitrite nor the dicumyl hyponitrite were available commercially. They were therefore synthesized.

Di-tert-butyl Hyponitrite Synthesis

The synthesis closely followed a literature procedure⁴⁷. First, 5 mL of *tert*-butyl bromide was placed in a beaker that has been cooled to 0°C by using an ice-water bath. Then 1.0 g of dry silver hyponitrite was added slowly, in small portions. After 15 minutes of continuous stirring, the AgBr was filtered off and washed with ether. The filtrates were combined and roto-evaporated. The residue was recrystallized from methanol and dried over P₂O₅ for 1 hour.

Dicumyl Hyponitrite Synthesis

The synthesis closely followed a literature procedure⁴⁸. Cumyl chloride was first synthesized by bubbling HCl gas through 8 mL of cumyl alcohol in dichloromethane. The bottom layer of cumyl chloride was pipetted into a clean beaker that has been cooled to 0°C by using an ice-water bath. Then 1.0 g of dry silver hyponitrite was added slowly, in small portions. After 20 minutes of continuous stirring, the AgCl was filtered off and washed with ether. The filtrates were combined and roto-evaporated. The residue was recrystallized from methanol and dried over P₂O₅ for 1 hour.

2.2 Laser Flash Photolysis (LFP)

The equipment involved in LFP was been previously reviewed under Apparatus (Section 1.3). *Tert*-butoxyl and cumyloxyl radicals were generated by 308 nm LFP of solutions which generally contained 0.22 M di-*t*-butyl peroxide or 0.13 M dicumyl peroxide, respectively (these concentrations give an O.D. ~0.3 at the laser wavelength in

the 7x7 mm² Suprasil quartz cell). All solutions of peroxide, borane ($\text{Et}_3\text{N} \rightarrow \text{BH}_3$ or $n\text{-Bu}_4\text{N}^+\text{BH}_4^-$) and, when required, an added reagent at a known concentration were deoxygenated by purging with nitrogen for > 5 min prior to flashing with the laser. Pseudo-first-order rate constants (k_{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_3^- growth or decay), at 375 nm ($\text{Et}_3\text{N} \rightarrow \text{BH}_2^+$ growth or decay), or at 321 nm (benzylic radicals growth). A plot of the experimental rate constants, k_{exptl} , against the concentration of the substrate (using at least five different substrate concentrations) should give a straight lines in all cases and the slopes of these lines are, of course, equal to the desired rate constants, k , viz., $k_{\text{exptl}} = k_0 + k[\text{Substrate}]$, where k_0 is the rate constant for all first order and *pseudo*-first order reactions in the absence of substrate. The absolute second-order rate constants (k) were found by least squares fitting the plots of k_{exptl} vs. [substrate].

2.3 Cumyloxyl Radical Reactions with $\text{Et}_3\text{N} \rightarrow \text{BH}_3$ in Pyridine

Dicumyl hyponitrite was decomposed at 298 K in the dark for 10 days (15 half-lives of dicumyl hyponitrite⁴⁸) in nitrogen-purged pyridine in sealed Pyrex vessels containing seven different concentrations of either $\text{Et}_3\text{N} \rightarrow \text{BH}_3$ 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 x 0.02 mm (i.d.) 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 (the half life of the dicumyl hyponitrite is 16h⁴⁸). The kinetics of exchange were examined via decoupled ¹¹B NMR (128.4 MHz, Bruker DRX400, 80.42% ¹¹B abundance which has spin 3/2) by monitoring the decay of the Et₃N→BH₃ peak (13.5 ppm) and the grow-in of the C₅H₅N→BH₃ peak (12.1 ppm) against a reference standard (Et₂O•BF₃) as shown in the spectrum in Figure 2. At a concentration of 0.06 M Et₃N→BH₃ in neat pyridine which was comparable to those used in our cumyloxyl radical experiments (range of 0.01-0.08 M), pseudo-first order conditions will apply.

The solution was sealed in a special NMR sample tube made from boron-free material; quartz was used in these experiments. The sample tube was then purged with nitrogen gas and periodically, ¹¹B NMR spectra were obtained to give Et₃N→BH₃ and C₅H₅N→BH₃ concentrations at time, t. Therefore a plot of $\ln([Et_3N \rightarrow BH_3]_t / [Et_3N \rightarrow BH_3]_0)$ against time, t, should give a straight line (see Figure 3). The $[Et_3N \rightarrow BH_3]_t / [Et_3N \rightarrow BH_3]_0$ value was determined by dividing the Et₃N→BH₃ peak area (at time, t) by the initial Et₃N→BH₃ peak area (see data in Table 1). The plot did give a straight line ($r^2=0.98$) and its slope gave a pseudo-first order rate constant of $3.9 \times 10^{-6} \text{ s}^{-1}$ corresponding to $t_{1/2} = 50\text{h}$.

Figure 2 – 128.4 MHz decoupled ^{11}B NMR spectrum of 0.06 M $\text{Et}_3\text{N} \rightarrow \text{BH}_3$ in neat pyridine at a time of 28 h.

Figure 3 – Plot of $\ln([Et_3N \rightarrow BH_3]/[Et_3N \rightarrow BH_3]_0)$ vs. time to determine the rate constant for pyridine exchange with triethylamine $\rightarrow$ borane. Each point represents a single measurement and therefore is not given with error bars.

Table 1. Data for the plot of $\ln([Et_3N \rightarrow BH_3]_t/[Et_3N \rightarrow BH_3]_0)$ vs. time.

Time (s)	relative to the $Et_2O \cdot BF_3$ peak area		ratio	$\ln \left(\frac{[Et_3N \rightarrow BH_3]_t}{[Et_3N \rightarrow BH_3]_0} \right)$
	$Et_3N \rightarrow BH_3$ peak area	pyridine $\rightarrow BH_3$ peak area		
0	6.01	0.00	1.00	0.00
18000	5.43	0.57	0.90	-0.10
79200	4.79	1.20	0.80	-0.23
100800	3.86	2.18	0.64	-0.44
177730	3.20	2.81	0.53	-0.63
198000	2.44	3.57	0.41	-0.90
345600	1.77	4.24	0.30	-1.22
403200	1.09	4.93	0.18	-1.71
496800	0.98	5.03	0.16	-1.81
604800	0.69	5.31	0.12	-2.16
723600	0.31	5.70	0.05	-2.97

2.4 Competitive Kinetics of Halide Abstraction by $\text{Et}_3\text{N}\rightarrow\text{BH}_2$

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 12 mM $\text{Et}_3\text{N}\rightarrow\text{BH}_3$ together with *n*-PrBr and an alkyl chloride. The concentration of the hyponitrite was 0.5 mM, i.e., ca. 4% that of the $\text{Et}_3\text{N}\rightarrow\text{BH}_3$ and since nearly two freely diffusing *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 $\text{Et}_3\text{N}\rightarrow\text{BH}_2\text{Br}$ and $\text{Et}_3\text{N}\rightarrow\text{BH}_2\text{Cl}$ were very roughly equal ($[\text{RCl}]$ varied from 0.1 to 3 M).

The solution was sealed in a special non-Boron containing NMR tube that was then purged with nitrogen gas. A ^{11}B NMR was taken periodically (more often in the beginning) and the relative yields of these two products were measured: BCl (-5.5 ppm) and BBr (-8.0 ppm) both relative to (added) $\text{Et}_2\text{O}\bullet\text{BF}_3$. The BCl:BBr ratios taken over the 10 day time period were averaged and used to calculate the alkyl chloride/alkyl bromide halogen abstraction rate constant ratio.

2.5 Theoretical Calculations

For both the dipole moment and the electron affinity calculations, the AM1⁴⁹ semi-empirical method was used to optimize the geometry of the molecule being examined. These AM1 geometries were then used to calculate the dipole moment and the

single point energies which were computed using the B3LYP functional^{50,51} with the 6-311+G(2d, 2p) basis set.

The electronic energies and zero-point energies were summed to give E_0 , the total energy at 0 K. The electron affinities were calculated as E_0 (anion) - E_0 (parent). The validity of the calculated EA value for $\text{C}_6\text{F}_5\text{CH}=\text{CH}_2$ was checked by calculations on various $\text{C}_6\text{H}_5\text{X}$ and $\text{C}_6\text{F}_5\text{X}$ compounds for which experimental EA values were also available⁵² (see Table 2). All calculations were performed using the Gaussian 98 package⁵³.

Table 2. Comparison of calculated (B3LYP/6-311+G(2d, 2p)//AM1) and experimental electron affinities for some C_6H_5X and C_6F_5X compounds.

Substrate	Calcd. EA/eV	Expt. EA/eV ^a
$C_6H_5O^\bullet$	2.20	2.25
$C_6F_5O^\bullet$	3.19	3.34
$C_6H_5^\bullet$	1.01	1.01
$C_6F_5^\bullet$	2.59	2.7
C_6H_5CN	0.25	0.26
C_6F_5CN	1.05	1.08
$C_6H_5COCH_3$	0.35	0.33
$C_6F_5COCH_3$	0.96	0.88
$C_6H_5CH=CH_2$	-0.20	-0.25 ^b
$C_6F_5CH=CH_2$	0.51	^c

^a From reference 52 unless otherwise noted. ^b Reference 54. ^c Not available.

3 Results

3.1 UV-Visible Spectra of $\text{Et}_3\text{N}\rightarrow\text{BH}_2^\bullet$ and $\text{BH}_3^{\bullet-}$

To monitor the $\text{Et}_3\text{N}\rightarrow\text{BH}_2^\bullet$ and $\text{BH}_3^{\bullet-}$ radicals by UV-Vis, spectra were required and none had been previously published. LFP, at 308 nm, of a solution of 4 % (v/v) di-*tert*-butyl peroxide in benzene containing $\text{Et}_3\text{N}\rightarrow\text{BH}_3$ (44 mM) or $n\text{-Bu}_4\text{N}^+\text{BH}_4^-$ (24 mM) produced these spectra (recorded at 10 nm intervals from 320 to 600 nm) shown in Figures 4 and 5 which are assigned to $\text{Et}_3\text{N}\rightarrow\text{BH}_2^\bullet$ and $\text{BH}_3^{\bullet-}$, respectively. Although these spectra are almost featureless, they do allow kinetic data for reactions of these two radicals with added substrates when the substrate-derived radical has no absorption in the visible or near UV regions of the spectrum.

3.2 Kinetics of the Reactions of *tert*-Alkoxy Radicals with $\text{Et}_3\text{N}\rightarrow\text{BH}_3$ and BH_4^- in Benzene

The absolute rate constants for hydrogen 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 O. D. of ca. 0.3 at the 308 nm laser wavelength in the 7 x 7 mm² quartz LFP cell. The alkoxy radicals were generated "instantaneously" in the laser pulse.

Figure 4 – Transient absorption spectrum of $\text{Et}_3\text{N} \rightarrow \text{BH}_2^+$ in di-*t*-butyl peroxide / benzene (4:96, v/v) measured 1.2 (filled circles), 4.4 (open circles) and 6.4 μs (open squares) after the laser pulse.

Figure 5 – Transient absorption spectrum of BH_3^+ in di-*t*-butyl peroxide / benzene (4:96, v/v) measured 4.4 (filled circles), 8.0 (open circles) and 16.0 μs (open squares) after the laser pulse.

Since *tert*-butoxyl radicals have no absorption in the near UV-visible,⁵⁵ the pseudo-first-order grow-ins, k_{exptl} , of the absorptions due to $\text{Et}_3\text{N} \rightarrow \text{BH}_2^\bullet$ and $\text{BH}_3^{\bullet-}$ were monitored at 375 nm and 475 nm, respectively.

However, cumyloxyl radicals have a fairly strong absorption in the visible, $\lambda_{\text{max}} = 485 \text{ nm}$,⁵⁵ and for $\text{Et}_3\text{N} \rightarrow \text{BH}_3$ in this case the pseudo-first-order decay (k_{exptl}) of cumyloxyl was monitored. However, with BH_4^- and dicumyl peroxide the LFP experiment produced a growth at 485 nm (which confirms the high extinction coefficient of $\text{BH}_3^{\bullet-}$). In this case, the rate constant for reaction 22 was obtained by monitoring the growth in the absorbance at 375 nm.

Measurements of k_{exptl} were made over a range of $\text{Et}_3\text{N} \rightarrow \text{BH}_3$ and BH_4^- concentrations.

It has been commonly assumed that all *tert*-alkoxyl radicals have equal reactivities in H-atom abstractions. My experimental data seems to show that this assumption is not completely accurate. In benzene for H-atom abstraction from $\text{Et}_3\text{N} \rightarrow \text{BH}_3$: $k_{19} = (5.34 \pm$

$0.06) \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (mean of four experiments, $\pm 1 \sigma$) and $k_{21} = (4.0_1 \pm 0.08) \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (mean of two experiments, $\pm 1 \sigma$). Similarly, in benzene for hydrogen atom abstraction from BH_4^- : $k_{20} = (6.1_7 \pm 0.09) \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $k_{22} = (5.2 \pm 0.1) \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (mean of two experiments, $\pm 1 \sigma$).

3.3 Kinetic Solvent Effects (KSEs) on Hydrogen Atom Abstraction from $\text{Et}_3\text{N} \rightarrow \text{BH}_3$ by the Cumyloxyl Radical

There are no significant KSEs for H-atom abstraction from saturated hydrocarbons (such as cyclohexane)²⁶. However, there are very large KSE's in hydrogen bond accepting (HBA) solvents for H-atom abstractions from substrates such as *tert*-butyl hydroperoxide, phenol and α -tocopherol which are fairly strong HBDs^{26,27,41,56}. Rate constants for H-atom abstraction from such hydroxylic substrates, $k_{\text{XOH}\cdot}^{\text{S}}$, decrease as the solvent, S, becomes a stronger HBA and, in fact, for each XOH substrate there is a linear correlation between $\log k_{\text{XOH}\cdot}^{\text{S}}$ and Abraham *et al.*'s⁵⁷ β_2^{H} scale of solvent HBA abilities^{39,56}. Although the borohydridic 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 21 seemed worth investigating because Lucarini *et al.*³² had reported that k_{19} is 5 times larger in pyridine than in *tert*-butylbenzene. Since pyridine ($\beta_2^{\text{H}} = 0.62$)⁵⁷ is a much stronger HBA than *tert*-butylbenzene (for which β_2^{H} has not been reported but is probably similar to toluene, $\beta_2^{\text{H}} = 0.14$)⁵⁷ the results of Lucarini *et al.*³²

would imply that k_{19} (and k_{21}) 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).⁵⁸

The results of the LFP direct measurements of k_{21} in 10 solvents are given in Table 5. Unfortunately, pyridine absorbs too strongly at the laser wavelength to be used as a solvent in LFP experiments. Therefore cumyloxyl radicals were generated by the thermal decomposition of dicumyl hyponitrite at 25 °C in the dark⁴⁸ in pyridine containing 7 different concentrations of $Et_3N \rightarrow BH_3$ and after 10 days (15 half-lives of the hyponitrite), as shown in reaction 23. The cumyloxyl radical will then either abstract a hydrogen from $Et_3N \rightarrow BH_3$ to yield cumyl alcohol as in reaction 21, or undergo a β -scission to yield acetophenone and a methyl radical (reaction 24). The relative yields of cumyl alcohol and acetophenone were then measured, allowing k_{21} to be derived, once k_{24} is known. Since the GC calibration curves for $PhCMe_2OH$ and $PhCOMe$ had the same slope, the area of the $PhCMe_2OH$ peak can be divided directly by the area of the $PhCOMe$ peak to determine $[PhCMe_2OH]/[PhCOMe]$ (see Table3).

Figure 6 – Ratio of [cumyl alcohol]/[acetophenone] vs $[\text{Et}_3\text{N} \rightarrow \text{BH}_3]$.

Table 3. Ratio of [cumyl alcohol]/[acetophenone] vs $[\text{Et}_3\text{N} \rightarrow \text{BH}_3]$ for reaction 21 over reaction 24.

$[\text{Et}_3\text{N} \rightarrow \text{BH}_3]$ (M)	PhCMe ₂ OH 10 ⁴ peak area	PhCOMe 10 ⁴ peak area	$\frac{[\text{PhCMe}_2\text{OH}]}{[\text{PhCOMe}]}$
0.05	84	336	0.25
0.1	130	309	0.42
0.2	160	193	0.83
0.3	220	180	1.22
0.4	251	162	1.55
0.5	272	143	1.90
0.6	313	133	2.35

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 $k_{21}/k_{24} = 92 \text{ dm}^3 \text{ mol}^{-1}$, as shown in Figure 6.

Since k_{24} also varies with solvent²⁶, its magnitude was determined in pyridine using cyclohexane as the H-atom donor to the cumyloxyl radical because H-atom abstraction from cyclohexane is known to be solvent independent²⁶.

Again the area of the PhCMe_2OH and PhCOMe peaks were used directly to give $[\text{PhCMe}_2\text{OH}]/[\text{PhCOMe}]$ (see Table 4). These alcohol/acetophenone ratios were plotted against various $[c\text{-C}_6\text{H}_{12}]$ to give an excellent straight line ($r^2 = 1.00$) with a slope which yields $k_{25}/k_{24} = 3.8 \text{ dm}^3 \text{ mol}^{-1}$, see Figure 7.

Since $k_{25} = 1.2 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$,²⁰ we obtain $k_{24} = 3.2 \times 10^5 \text{ s}^{-1}$ and, hence, $k_{21}(\text{pyridine}) = 2.9 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. This value is listed in Table 5 after the data for the 10 solvents in which the reaction was studied by LFP.

Figure 7 – Ratio of [cumyl alcohol]/[acetophenone] vs $[c\text{-C}_6\text{H}_{12}]$.

Table 4. Ratio of [cumyl alcohol]/[acetophenone] vs [*c*-C₆H₁₂] for reaction 25 over reaction 24.

[<i>c</i> -C ₆ H ₁₂] (M)	PhCMe ₂ OH 10 ⁴ peak area	PhCOMe 10 ⁴ peak area	$\frac{[\text{PhCMe}_2\text{OH}]}{[\text{PhCOMe}]}$
0.01	243	206	1.18
0.02	299	153	1.95
0.03	340	120	2.84
0.04	372	101	3.70
0.06	381	68	5.60
0.07	397	61	6.49
0.08	410	54	7.64

Table 5. Ambient temperature absolute rate constants for H-atom abstraction from $\text{Et}_3\text{N} \rightarrow \text{BH}_3$ by cumyloxyl radicals in various solvents.

Solvent	$10^{-7}k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \text{ }^{\text{a}}$
1. isooctane	12 ± 1
2. CCl_4	8.8 ± 0.1
3. <i>t</i> -butylbenzene	7.9 ± 0.2
4. <i>t</i> -butanol	7.1 ± 0.1
5. benzene	$4.0 \pm 0.1 \text{ }^{\text{b}}$
6. ethyl acetate	3.7 ± 0.2
7. DMSO	3.2 ± 0.1
8. methyl acetate	3.0 ± 0.2
9. methyl formate	2.6 ± 0.3
10. acetonitrile	2.2 ± 0.1
11. pyridine	$2.9 \pm 0.1 \text{ }^{\text{c}}$

^a Average k from two separate sets of experiments with 1σ errors as determined by monitoring the pseudo-first order decay of LFP generated cumyloxyl radicals using five or more $\text{Et}_3\text{N} \rightarrow \text{BH}_3$ concentrations, unless otherwise noted. ^b Average of four separate sets of experiments. ^c Calculated from plots of [cumyl alcohol]/[acetophenone] vs. $[\text{Et}_3\text{N} \rightarrow \text{BH}_3]$, the cumyloxyl radicals being generated by thermal decomposition of dicumyl hyponitrite (see Experimental, Section I.2.3).

3.4 Halogen Atom Abstraction by $\text{Et}_3\text{N}\rightarrow\text{BH}_2^\bullet$ and $\text{BH}_3^{\bullet-}$

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 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_{26} and k_{27} (see Table 6).

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 6).

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 $\text{Et}_3\text{N}\rightarrow\text{BH}_2^\bullet$ 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}B NMR. This analytical procedure was first checked using benzyl chloride and *tert*-butyl chloride (see Figures 8 and 9, respectively). 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 6). Spectra for competitive experiments of *n*-propyl bromide with *n*-propyl chloride, *n*-butyl chloride, and cyclohexyl chloride are shown in Figures 10 through 12, respectively.

Table 6. Ambient temperature absolute rate constants for some halogen atom abstractions by $\text{Et}_3\text{N} \rightarrow \text{BH}_2^\bullet$ and $\text{BH}_3^{\bullet-}$ radicals in benzene (plus related data from the literature for trialkyl-silicon-, germanium- and tin-centered radicals).

	$10^6 k / \text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$				
	$\text{Et}_3\text{N} \rightarrow \text{BH}_2^\bullet$ ^a	$\text{BH}_3^{\bullet-}$ ^a	$\text{Et}_3\text{Si}^\bullet$ ^b	$\text{Bu}_3\text{Ge}^\bullet$ ^c	$\text{Bu}_3\text{Sn}^\bullet$ ^d
CCl_4	4400 ± 300	2000 ± 300	4600	310	-
CHCl_3	3300 ± 500	620 ± 30	250	-	-
PhCH_2Br	1700 ± 200^e	530 ± 40^f	2400	790	1500^g
$(\text{CH}_3)_3\text{CBr}$	230 ± 20	320 ± 20	1100	86	$145 (170)^c$
<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^h	46	$32^i (26)^c$
CH_2Cl_2	120 ± 20	110 ± 20	71	-	-
PhCH_2Cl	11 ± 4^j	30 ± 5^k	20	1.9	1.1
PhCH_2Cl	13 ± 3^l				
$(\text{CH}_3)_3\text{CCl}$	1.2 ± 0.3	-	2.5	< 0.05	0.027
$(\text{CH}_3)_3\text{CCl}$	1.4 ± 0.4^l	-	-	-	-
<i>c</i> - $\text{C}_6\text{H}_{11}\text{Cl}$	0.43 ± 0.08^l	-	-	-	0.0034
$\text{CH}_3(\text{CH}_2)_2\text{Cl}$	$0.51 \pm 0.08^{l,m}$	-	0.31^g	-	0.0015^i

^a 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_{grow} , are given in

footnotes. ^b C. Chatgililoglu, K. U. Ingold and J. C. Scaiano, *J. Am. Chem. Soc.*, 1982, *104*, 5123. ^c K. U. Ingold, J. Lusztyk and J. C. Scaiano, *J. Am. Chem. Soc.* 1984, *106*, 343. ^d 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. ^e $k_{\text{grow}} = (1600 \pm 500) \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. ^f $k_{\text{grow}} = (510 \pm 50) \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. ^g M. Anpo, R. Sutcliffe and K. U. Ingold, *J. Am. Chem. Soc.*, 1983, *105*, 3580. Reported value multiplied by 1.7. ^h n-Butyl halide. ⁱ n-Pentyl halide. ^j $k_{\text{grow}} = (10 \pm 5) \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. ^k $k_{\text{grow}} = (27 \pm 6) \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. ^l Competitive experiment with $\text{CH}_3(\text{CH}_2)_2\text{Br}$ analyzed by ^{11}B NMR. ^m For n-butyl chloride $k = (0.48 \pm 0.07) \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

Figure 8 – 128.4 MHz decoupled ^{11}B NMR spectrum of 12 mM $\text{Et}_3\text{N} \rightarrow \text{BH}_3$ in a solution of benzene containing 0.5 mM di-*t*-butyl hyponitrite, 10 mM *n*-propyl bromide and 0.1 M benzyl chloride.

Figure 9 – 128.4 MHz decoupled ^{11}B NMR spectrum of 12 mM $\text{Et}_3\text{N} \rightarrow \text{BH}_3$ in a solution of benzene containing 0.5 mM di-*t*-butyl hyponitrite, 10 mM *n*-propyl bromide and 1 M *tert*-butyl chloride.

Figure 10 – 128.4 MHz decoupled ^{11}B NMR spectrum of 12 mM $\text{Et}_3\text{N} \rightarrow \text{BH}_3$ in a solution of benzene containing 0.5 mM di-*t*-butyl hyponitrite, 10 mM *n*-propyl bromide and 3 M *n*-propyl chloride.

Figure 11 – 128.4 MHz decoupled ^{11}B NMR spectrum of 12 mM $\text{Et}_3\text{N} \rightarrow \text{BH}_3$ in a solution of benzene containing 0.5 mM di-*t*-butyl hyponitrite, 10 mM *n*-propyl bromide and 3 M *n*-butyl chloride.

Figure 12 – 128.4 MHz decoupled ^{11}B NMR spectrum of 12 mM $\text{Et}_3\text{N} \rightarrow \text{BH}_3$ in a solution of benzene containing 0.5 mM di-*t*-butyl hyponitrite, 10 mM *n*-propyl bromide and 2 M cyclohexyl chloride.

3.5 Addition Reactions of $\text{Et}_3\text{N}\rightarrow\text{BH}_2^\bullet$

LFP of 6% (v/v) di-*tert*-butyl peroxide/benzene containing 0.14M $\text{Et}_3\text{N}\rightarrow\text{BH}_3$ generating the $\text{Et}_3\text{N}\rightarrow\text{BH}_2^\bullet$ radical ‘instantaneously’. The decay of these radicals was monitored directly in the presence of at least 5 different substrate concentrations by following the pseudo-first-order decay of $\text{Et}_3\text{N}\rightarrow\text{BH}_2^\bullet$ (see Table 7). The substrates were 17 olefins, 2 nitriles and 1 acetylene with varying chemical properties and structures. Unfortunately, chlorinated olefins had to be 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}B NMR to occur, at least to some extent, by chlorine atom abstraction.

Table 7. Ambient temperature absolute rate constants for addition of $\text{Et}_3\text{N} \rightarrow \text{BH}_2^\bullet$ radicals to some unsaturated substrates in benzene.

Substrate	$10^{-6} k / \text{dm}^3 \text{mol}^{-1} \text{s}^{-1}^a$
$\text{C}_6\text{F}_5\text{CH}=\text{CH}_2$	240 ± 50
$(\text{C}_6\text{H}_5)_2\text{C}=\text{CH}_2$	320 ± 40
$\text{C}_6\text{H}_5\text{CMe}=\text{CH}_2$	41 ± 4
$\text{C}_6\text{H}_5\text{CH}=\text{CH}_2$	110 ± 60
$\text{MeOC(O)CMe}=\text{CH}_2$	170 ± 50
$\text{MeOC(O)CH}=\text{CH}_2$	540 ± 30
$\text{C}_6\text{H}_5\text{C}\equiv\text{N}$	7.0 ± 0.3
$(\text{EtO})_3\text{SiCH}=\text{CH}_2$	6.3 ± 0.6
$\text{Me}_3\text{SiCH}=\text{CH}_2$	2.1 ± 0.4
$\text{MeCO}_2\text{CH}=\text{CH}_2$	2.5 ± 0.4
$\text{C}_6\text{H}_5\text{CH}=\text{CHMe}$	2.3 ± 0.5
$\text{N}\equiv\text{CCH}_2\text{CH}=\text{CH}_2$	2.2 ± 0.4
$\text{HOCH}_2\text{CH}=\text{CH}_2$	1.1 ± 0.3
$\text{MeCO}_2\text{CMe}=\text{CH}_2$	1.2 ± 0.3
$\text{C}_6\text{H}_5\text{CH}_2\text{CH}=\text{CH}_2$	< 0.5
$\text{Me}_3\text{CCH}=\text{CH}_2$	< 0.5
$\text{EtOCH}=\text{CH}_2$	< 0.5
$\text{MeOCMe}=\text{CH}_2$	< 0.5
$\text{C}_6\text{H}_5\text{C}\equiv\text{CH}$	< 0.5
$\text{MeC}\equiv\text{N}$	< 0.5

^a Average k from two separate sets of experiments with 1 σ errors as determined by monitoring the decay of $\text{Et}_3\text{N} \rightarrow \text{BH}_2^\bullet$.

3.6 Hydrogen Atom Abstraction from Electron-Deficient C-H Groups

These hydrogen atom abstractions are important for PRC and its synthetic utility. However, only three H-atom donors were found which were sufficiently reactive to measure absolute rate constants, k_{28} , by LFP and monitoring the decay of the “instantaneously” generated $\text{Et}_3\text{N}\rightarrow\text{BH}_2^\bullet$ radical in the presence of at least 5 different substrate concentrations (see Table 8). For example, although the reaction of ethyl acetate with $\text{Me}_3\text{N}\rightarrow\text{BH}_2^\bullet$ is known to occur¹² the analogous reaction with $\text{Et}_3\text{N}\rightarrow\text{BH}_2^\bullet$ was too slow to measure by LFP.,

where EWG = electron-withdrawing group.

Hydrogen atom abstractions by $\text{BH}_3^{\bullet-}$ from all the H-atom donors listed in Table 8 were too slow to measure by LFP, i.e., $k \leq 5 \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

Table 8. Ambient temperature absolute rate constants for hydrogen atom abstraction from some electron-deficient C-H bonds by $\text{Et}_3\text{N} \rightarrow \text{BH}_2^\bullet$ in benzene.

Substrate	$10^{-6} k_{24} / \text{dm}^3 \text{mol}^{-1} \text{s}^{-1}^{\text{a}}$	Reactivities relative to n-PrBr = 100	
		$\text{Et}_3\text{N} \rightarrow \text{BH}_2^\bullet^{\text{b}}$	$\text{Me}_3\text{N} \rightarrow \text{BH}^\bullet\text{CMe}_2\text{CHMe}_2^{\text{c}}$
$\text{HC}(\text{CO}_2\text{Et})_3$	33 ± 3	16.5	19
$\text{H}_2\text{C}(\text{CO}_2\text{Et})_2$	12 ± 4	6.0	6.6
$\text{H}(\text{CH}_3)\text{C}(\text{CO}_2\text{Et})_2$	2.2 ± 0.3	1.1	0.3
$(\text{CH}_2\text{CO}_2\text{Et})_2$	$\leq 0.5^{\text{d}}$	-	0.03
$\text{H}_3\text{CCO}_2\text{Et}$	$\leq 0.5^{\text{d}}$	-	0.002

^a Average k from two separate sets of experiments as determined by monitoring the decay of $\text{Et}_3\text{N} \rightarrow \text{BH}_2^\bullet$ at five or more ester concentrations.

^b This work. ^c This was an ESR study done at 189 K in cyclopropane, which assumes that the products radicals were removed by diffusion-controlled reactions with equal rate constants¹¹. ^d Too slow to measure.

4 Discussion

4.1 UV-Visible Spectra of $\text{Et}_3\text{N} \rightarrow \text{BH}_2^\bullet$ and $\text{BH}_3^{\bullet-}$

The extensive, low temperature, ESR studies of Roberts and coworkers^{2-5,10-12,16-24} leave no doubt that the initial, i.e., kinetic, products of the reaction of *tert*-alkoxyl radicals with amine $\rightarrow$ boranes and the borohydride anion are amine $\rightarrow$ boryl radicals and the borane radical anion, respectively. For this reason, Figure 4 and 5 are assigned to $\text{Et}_3\text{N} \rightarrow \text{BH}_2^\bullet$ and $\text{BH}_3^{\bullet-}$, respectively. This is further supported by the absolute rate constant measurements based mainly on monitoring the decay of the transient absorptions shown in Figures 4 and 5, giving kinetic data that are fully congruent with the results of the ESR experiments.

4.2 Kinetics of the Reactions of *tert*-Alkoxyl Radicals with $\text{Et}_3\text{N} \rightarrow \text{BH}_3$ and BH_4^- in Benzene

As expected, the *tert*-butoxyl and cumyloxyl radicals were excellent hydrogen atom abstractors from the triethylamine $\rightarrow$ borane complex and the borohydride anion. However, the slightly lower reactivity of cumyloxyl in H-atom abstraction from these two boranes (ca. 80%) compared with *tert*-butoxyl was not expected since it has been tacitly assumed that these two alkoxyls are equally reactive³¹. This decrease in reactivity of

cumyloxyl could arise from several causes, such as a greater steric hindrance of the radical center or the inductive effect of the phenyl group. However, it seems logical 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 which gives rise to cumyloxyl's visible absorption band⁵⁵, viz.,

This absorption band of the cumyloxyl radical, shown in Figure 13 (filled circles), has an extinction coefficient, ϵ_{485} , that has been estimated⁵⁵ at approximately $1300 \text{ M}^{-1} \text{ cm}^{-1}$. One can also clearly see that this absorption band does not occur in the *tert*-butoxyl radical spectrum (open circles in Figure 13).

It has also been found that the borohydride anion is about 10 times as reactive as triethylamine→borane towards *tert*-alkoxyl radicals in benzene at room temperature, as the rate constants show; $k_{22} = 5.2 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $k_{21} = 4.0 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (rate constants for the hydrogen atom abstraction by the cumyloxyl radical from the borohydride anion and the triethylamine→borane complex, respectively).

Figure 13 – Transient absorption spectrum of the cumyloxyl (filled circles) and *tert*-butoxyl (open circles) radical in benzene measured 4.4 μ s after the laser pulse.

4.3 Kinetic Solvent Effects (KSEs) on Hydrogen Atom Abstraction from $\text{Et}_3\text{N}\rightarrow\text{BH}_3$ by the Cumyloxyl Radical

I am not aware of any earlier kinetic data for the generation of the borane radical anion or its successive reactions. However, for the generation of the $\text{Et}_3\text{N}\rightarrow\text{BH}_2^\bullet$ radical generated by *tert*-butoxyl radicals, Lucarini *et al.*³² reported $k_{19} = 2.6 \times 10^7$ and 13×10^7 $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ at 25 °C in *tert*-butylbenzene and pyridine, respectively. These workers used a competitive kinetic procedure. *Tert*-butoxyl radicals were generated by photolysis of di-*tert*-butyl peroxide in the presence of $\text{Et}_3\text{N}\rightarrow\text{BH}_3$ and Ph_3SiH 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 rates of consumption of $\text{Et}_3\text{N}\rightarrow\text{BH}_3$ and the silane yielded k_{19} . The value they obtained for k_{19} in *tert*-butylbenzene (2.6×10^7) 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 5). However, their value in pyridine (13×10^7) appeared to be anomalous because our results showed that k_{19} decreased in more polar solvents (Table 5) rather than increasing.

Since the direct measurement of k_{19} or k_{21} by 308 nm 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 β -scission of cumyloxyl (yielding acetophenone). This procedure gave $k_{21} = 2.9 \times 10^7 \text{ dm}^3 \text{mol}^{-1} \text{s}^{-1}$ in pyridine which is a factor of 4.5 lower than Lucarini *et al.*'s estimate of k_{21} . However, as these authors recognized, there is always the potential for ligand exchange when an aliphatic amine $\rightarrow$ 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.³² Exchange

becomes much more likely on the time scale of this experiment (50% reaction in 16h).

Therefore ^{11}B NMR was used to monitor reaction 27 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 50h. Clearly, the major reaction monitored in my experiments in pyridine was hydrogen atom abstraction from $\text{Et}_3\text{N}\rightarrow\text{BH}_3$, not abstraction from $\text{C}_5\text{H}_5\text{N}\rightarrow\text{BH}_3$. If exchange did occur, 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 $\text{C}_5\text{H}_5\text{N}\rightarrow\text{BH}_2^\bullet$ into the pyridine ring. Hydrogen atom abstraction would therefore be expected to be faster from the pyridine complex than from the triethylamine complex.

That hydrogen abstraction (from $\text{Et}_3\text{N}\rightarrow\text{BH}_3$) is *slower* in pyridine than in *tert*-butylbenzene is consistent with the trend observed in the LFP experiments which show that k_{21} decreases as the solvents become more polar. Furthermore, because relative rate constant measurements made in competitive kinetic experiments are intrinsically less accurate when reactant loss is monitored (as in ref. 32) than when product formation is followed (as in this work), my rate constant (k_{21}) is probably more reliable than Lucarini's (k_{19}).

Although the $\text{Et}_3\text{N}\rightarrow\text{BH}_2^\bullet$ radical reacts extremely rapidly with some of the solvents listed in Table 5 (e.g., CCl_4 , see Table 6) this does not interfere with

measurements of k_{21} because these are based on rates of decay of the cumyloxyl radicals as a function of $[\text{Et}_3\text{N} \rightarrow \text{BH}_3]$.

4.4 Kinetic Solvent Effects Correlated with Empirical Solvent Parameters

In any analysis of solvent effects on chemical reactions, it is customary to seek a linear relationship between some empirical solvent parameter and the logarithm of the rate constant for a reaction, i.e., a linear free energy relationship.⁴² The logarithm of the rate constant for the hydrogen atom abstraction from $\text{Et}_3\text{N} \rightarrow \text{BH}_3$ by cumyloxyl radicals was plotted against many different empirical solvent parameter; the two that are included here are β_2^{H} and $E_{\text{T}}(30)$ (see Table 9).

The effect of solvents on this reaction correlate rather poorly with Abraham's⁵⁷ β_2^{H} (HBA accepting) parameter, (see Figure 14, the least squares line yields $r^2 = 0.45$, or 0.58 if the point for *tert*-butanol is ignored) and not much better with various other solvent polarity parameters such as Dimroth and Reichardt's $E_{\text{T}}(30)$ parameters⁴² which reflect the effects of local ordering of solvent molecules in the cybotactic region around a polar solute (see Figure 15, the least squares lines yields $r^2 = 0.57$, or 0.79 if the point for *tert*-butanol is ignored). The $E_{\text{T}}(30)$ values do not measure the polarity of the bulk solvent mixture, but rather the micropolarity of the solvent shell around the solute. If a solvent polarity parameter is to be used to correlate the effects of solvents on the reaction rate, then it is essential that the parameter reflects the properties of the cybotactic region, because reaction rates are molecular properties and will be more strongly influenced by the local effects of the solvent in the cybotactic region.

Table 9. Ambient temperature absolute rate constants for H-atom abstraction from $\text{Et}_3\text{N} \rightarrow \text{BH}_3$ by cumyloxyl radicals in various solvents and the empirical parameters β_2^{H} and $E_{\text{T}}(30)$ which reflect certain properties of these solvents.

Solvent	$\text{Log} (k_{\text{Et}_3\text{N} \rightarrow \text{BH}_3 / \text{CumO}^\bullet}^{\text{S}} / \text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1})$	β_2^{H} ^a	$E_{\text{T}}(30)$ ^b
1. isooctane	8.08	0.00	31.0
2. CCl_4	7.94	0.05 ^c	32.4
3. <i>t</i> -butylbenzene	7.90	0.14 ^d	33.9 ^d
4. <i>t</i> -butanol	7.85	0.49	43.3
5. benzene	7.60	0.14	34.3
6. ethyl acetate	7.57	0.45	38.1
7. DMSO	7.51	0.78	45.1
8. methyl acetate	7.48	0.40	40.0
9. methyl formate	7.42	0.38	45.0
10. acetonitrile	7.34	0.44	45.6
11. pyridine	7.46	0.62	40.5

^a Reference 57 unless otherwise noted. ^b Units are kcal mol^{-1} , reference 42.

^c Reference 56. ^d Not available, therefore assumed to be the same as for toluene.

Clearly these KSE do not depend solely on the ability of the solvent to accept a hydrogen bond nor on the polarity of the solvent. However, it is not expected that an empirical solvent scale based on a particular reference process is universal and useful for all kinds of reactions.⁴² Any comparison of the effect of solvent on a process of interest with a solvent polarity parameter is, in fact, a comparison with a reference process.

The most deviant behavior in Figures 14 and 15 is observed in *tert*-butanol. In this solvent, k_{21} is smaller than in isooctane or CCl_4 but is larger than would be predicted from *tert*-butanol's β_2^H or $E_T(30)$ values. Similar anomalous KSEs in *tert*-butanol (i.e., larger rates than would be predicted from this solvent's β_2^H value) have been encountered in a number of other H-atom abstraction reactions.^{41,59,60} It has been found that this is not a general property of alcohols but appears to be confined to the more sterically demanding alcohols, particularly *tert*-butanol⁵⁹ and I can add no further insight into this rate "enhancement".

It should, perhaps, be noted that the KSEs can be useful since they can be used to direct reactions down chosen pathways. For example, *tert*-butoxyl radicals generated from the catalytic decomposition of *tert*-butyl hydroperoxide in the presence of cyclohexane can either preferentially abstract a hydrogen atom from the alkane (when the reaction is carried out in a strong hydrogen bond accepting solvent) or the hydroperoxide (when in a poor hydrogen bond accepting solvent).⁶¹ As one example where the reaction pathway was affected by the hydrogen bond *accepting* ability of the solvent is the work of Minisci and coworkers on the oxidation of α -methylstyrene by *tert*-butyl

Figure 14 - $\text{Log} (k_{Et,N \rightarrow BH_3/CumO^\bullet}^S / \text{dm}^3 \text{mol}^{-1} \text{s}^{-1})$ vs. β_2^H . The numbers beside the points correspond to the solvents indicated in Table 9. 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 *t*-butanol (4), see text.

Figure 15 - $\text{Log} (k_{E_T N \rightarrow BH_3 / CumO}^S / \text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1})$ vs. $E_T(30) / \text{kcal mol}^{-1}$. The numbers beside the points correspond to the solvents indicated in Table 9. 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 *t*-butanol (4), see text.

hydroperoxide catalyzed by Fe(III).⁶² When the reaction is done in benzene, the major product is **1**, but in pyridine, a strong hydrogen bond acceptor, **2** becomes the main product. The ability to alter products by changing the solvent represents an important achievement in free radical chemistry. Although the rate constants in this work do not vary much with solvent, they may provide a new and useful tool for synthetic organic chemists.

4.5 β -Scission of $\text{Et}_3\text{N}\rightarrow\text{BH}_2^\bullet$

The bane of the $\text{Et}_3\text{N}\rightarrow\text{BH}_2^\bullet$ radical is that it decays quite rapidly with first-order kinetics 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 β -scission:

The potential alternative consumption of $\text{Et}_3\text{N}\rightarrow\text{BH}_2^\bullet$ by hydrogen atom abstraction in saturated hydrocarbons, e.g., isooctane was essentially eliminated by

showing that the rate constant for $\text{Et}_3\text{N} \rightarrow \text{BH}_2^\bullet$ 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 also identical to its value in isooctane.

The rate constants for β -scission of amine $\rightarrow$ boryl radicals are expected to be greatest in saturated hydrocarbon solvents and to decrease as the solvent becomes more polar, because $\text{R}_3\text{N} \rightarrow \text{BH}_2^\bullet$ radicals have large dipole moments (5.3 D calculated⁵³ for $\text{Et}_3\text{N} \rightarrow \text{BH}_2^\bullet$, cf. 5.7 D for $\text{H}_3\text{N} \rightarrow \text{BH}_2^\bullet$ ²¹) which are larger than those of the $\text{R}_2\text{N} \rightleftharpoons \text{BH}_2$ product (2.0 D calculated⁴¹ for $\text{Et}_2\text{N} \rightleftharpoons \text{BH}_2$).

Analogous β -scission reactions have been shown by Roberts and coworkers^{3,63} using ESR spectroscopy to be facile processes even at considerably lower temperatures. For example, in the competitions:

$k_{31}/k_{33} = 0.03$ and $k_{32}/k_{33} = 0.05 \text{ mol dm}^{-3}$ at 255 K.³ Reactions 31 and 32 have also been monitored directly by time resolved ESR spectroscopy over a range of temperatures.⁶³ It can be calculated from the Arrhenius parameters that at 25 °C, $k_{31} = 6.3 \times 10^6 \text{ s}^{-1}$ and $k_{32} = 1.6 \times 10^7 \text{ s}^{-1}$ in the solvent mixtures employed (cyclopropane, *t*-alcohols containing di-*t*-butyl peroxide). These two β -scission rate constants are consistent with my measured

rate constant for decay of $\text{Et}_3\text{N} \rightarrow \text{BH}_2^\bullet$ in isooctane and benzene corresponding also to a β -scission, reaction 30.

4.6 Halogen Atom Abstraction by $\text{Et}_3\text{N} \rightarrow \text{BH}_2^\bullet$ and $\text{BH}_3^{\bullet-}$

The $\text{Et}_3\text{N} \rightarrow \text{BH}_2^\bullet$ and $\text{BH}_3^{\bullet-}$ radicals have rather similar reactivities in halogen atom abstractions, though the latter radical seems to be slightly more reactive than the former towards some of the less reactive halides (as previously suggested for Br abstraction from *n*-PrBr).² Roberts and coworkers have previously reported that the relative rates of halogen atom abstraction from the $\text{Me}_3\text{CBr}/n\text{-PrBr}$ pair by $\text{Et}_3\text{N} \rightarrow \text{BH}_2^\bullet$ is 1.2 ± 0.1 at 246 K³ (cf., a 1.7₇ ratio at ca. 298 K from Table 6) and for the $\text{Me}_3\text{CCl}/n\text{-PrCl}$ pair by $\text{Me}_3\text{N} \rightarrow \text{BH}_2^\bullet$ is 5.0 at 261 K¹⁰ (cf., a ratio of ca. 2.6, Table 6). Roberts' two rate constant ratios and the two from this work are in gratifying agreement considering the differences in temperature and the different experimental procedures by which they were obtained (ESR^{3,10}, LFP and ¹¹B NMR). Table 6 also allows 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. This data supports a previous tentative conclusion by Green and Roberts²⁰ that it seemed likely that the absolute reactivities of the amine-boryls towards alkyl halides were broadly similar to those of trialkylsilyl radicals. However, at the low temperatures used in the ESR experiments it was found that $\text{Me}_3\text{N} \rightarrow \text{B}^\bullet\text{HBu}^n$ abstracts chlorine much more rapidly from

1-chlorobutane than does $\text{Et}_3\text{Si}^\bullet$,¹² as well as, being more selective than $\text{Et}_3\text{Si}^\bullet$ in competitive abstraction of chlorine from $n\text{-BuCl}$ and $(\text{MeO})_n\text{CH}_2\text{-CH}_2\text{Cl}$.²³ The rate enhancing effect of the β -oxygen at 200 K on chlorine abstraction by $\text{Me}_3\text{N} \rightarrow \text{B}^\bullet\text{HBu}^\bullet$ (factor of 30–45 for $n=3/n=0$) and $\text{Et}_3\text{N} \rightarrow \text{BH}_2^\bullet$ (factor of 17 for $n=3/n=0$) is not reflected by $\text{Et}_3\text{Si}^\bullet$ (factor of only 2.3 - 2.4 for $n=3/n=0$).²³ This indicates the importance of polar effects in reducing the activation energy for halogen atom abstraction by stabilizing the transition state through charge separation, eg., $[(\text{RCH}_2^\bullet \text{Cl}^- \text{ } ^+\text{X}) \leftrightarrow (\text{RCH}_2^- \text{Cl}^\bullet \text{ } ^+\text{X})]^\ddagger$. This also means the greater the electron affinity of the halogen atom donor ($\text{RCH}_2^\bullet$), the greater the transition state stabilization.

4.7 Addition Reactions of $\text{Et}_3\text{N} \rightarrow \text{BH}_2^\bullet$

The absolute rate constants for addition of the $\text{Et}_3\text{N} \rightarrow \text{BH}_2^\bullet$ radical to some unsaturated substrates, shown in Table 7 are congruent with the ESR studies by Roberts and coworkers. Table 7 is a collection of many different alkenes, a couple of nitriles and an alkyne, all with a wide range of chemical and physical properties. Although these reactions are not likely to be of much synthetic utility, their rate constants provide further insight into the nucleophilicity of the $\text{Et}_3\text{N} \rightarrow \text{BH}_2^\bullet$ radical.

4.7.1 Fischer's Quantitative Analysis of Nucleophilicity

The nucleophilic $\text{Et}_3\text{N} \rightarrow \text{BH}_2^\bullet$ radical seems, in the absence of steric effects, to add more rapidly to those olefins which are more electron-deficient. Such behavior has been observed previously by Fischer and coworkers for addition of the nucleophilic benzyl,^{64,65} hydroxymethyl,⁶⁶ *tert*-butyl⁶⁷ and 2-hydroxyprop-2-yl⁶⁸ radicals to various mono- and 1,1-di-substituted olefins.[†] Indeed, for each of these carbon-centered radicals Fischer and coworkers found that there is a linear correlation between $\log (k_{\text{add}}^{\text{R}^\bullet} / \text{dm}^3 \text{mol}^{-1} \text{s}^{-1})$ and the electron affinity of the olefins as indicated by equation 34.

Figure 16 shows the linear correlation of the benzyl⁶⁵ and *tert*-butyl radicals⁶⁷, as previously shown by Fischer and coworkers. Although these plot do not show the best correlation ($R^2 = 0.78$ and $R^2 = 0.81$ for benzyl and *tert*-butyl radicals, respectively), one can see that there is a definite increase in the logarithm of the addition rate constant with an increase in electron affinity of the substrate.

[†] 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.⁶⁹

Figure 16 - $\text{Log}(k_{\text{add}}^{R^\bullet} / \text{dm}^3 \text{mol}^{-1} \text{s}^{-1})$ vs. EA/eV . The filled circles represent the *tert*-butyl radical and the open circles are the benzyl radical.

4.7.2 Nucleophilicity of $\text{Et}_3\text{N} \rightarrow \text{BH}_2^\bullet$

To analyze the nucleophilicity of $\text{Et}_3\text{N} \rightarrow \text{BH}_2^\bullet$, mono-substituted and 1,1-disubstituted olefins which would be expected to undergo exclusive, or almost exclusive, addition with $\text{Et}_3\text{N} \rightarrow \text{BH}_2^\bullet$ were chosen and rate constants for these addition reactions were determined.

A plot of $\log (k_{\text{add}}^{\text{Et}_3\text{N} \rightarrow \text{BH}_2^\bullet})$ vs. the EA of the olefin is shown in Figure 17 and, as expected,⁶⁴⁻⁶⁸ there is a lot of scatter in this plot. However, it is clear that the rate constants generally increase as the EA increases, but since $\text{Et}_3\text{N} \rightarrow \text{BH}_2^\bullet$ is so strongly nucleophilic, it reacts at or close to the diffusion-controlled rate with olefins having $\text{EA} \geq -0.5$ eV (i.e., $k_{\text{add}}^{\text{Et}_3\text{N} \rightarrow \text{BH}_2^\bullet} = 10^8 - 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$). The α -methylstyrene (3) rate constant is lower than "expected" for the addition of $\text{Et}_3\text{N} \rightarrow \text{BH}_2^\bullet$, which can probably be attributed to the fact that the double bond is twisted out of the phenyl ring plane in this olefin.⁷⁰ This twisting also occurs, to some extent, to the 1,1-diphenylethylene (2) and pentafluorostyrene (1).⁷⁰

Unfortunately all the alkenes with electron affinities known to be between -0.5 and -1.0 eV contain chlorine which was also abstracted. When the olefin's EA drops to below -1.0 eV the k_{add} drop below $10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and the addition reactions could, again, be easily monitored by LFP. The decline in $k_{\text{add}}^{\text{Et}_3\text{N} \rightarrow \text{BH}_2^\bullet}$ as the olefins' EA decrease from -0.5 to -1.5 eV is about two orders of magnitude and the decrease in $k_{\text{add}}^{\text{Et}_3\text{N} \rightarrow \text{BH}_2^\bullet}$ appears to be

Table 10. Ambient temperature absolute rate constants for addition of $\text{Et}_3\text{N} \rightarrow \text{BH}_2^\bullet$ radicals to some unsaturated substrates in benzene.

	Substrate	EA/eV ^a	Log ($k_{\text{add}}^{\text{Et}_3\text{N} \rightarrow \text{BH}_2^\bullet} / \text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$)
1.	$\text{C}_6\text{F}_5\text{CH}=\text{CH}_2$	0.51 ^b	8.4
2.	$(\text{C}_6\text{H}_5)_2\text{C}=\text{CH}_2$	0.36 ^c	8.5
3.	$\text{C}_6\text{H}_5\text{CMe}=\text{CH}_2$	- 0.23	7.6
4.	$\text{C}_6\text{H}_5\text{CH}=\text{CH}_2$	- 0.25	8.0
5.	$\text{MeOC(O)CMe}=\text{CH}_2$	- 0.38 ^c	8.2
6.	$\text{MeOC(O)CH}=\text{CH}_2$	- 0.49	8.7
7.	$(\text{EtO})_3\text{SiCH}=\text{CH}_2$	- 1.11	6.8
8.	$\text{Me}_3\text{SiCH}=\text{CH}_2$	- 1.14	6.3
9.	$\text{MeCO}_2\text{CH}=\text{CH}_2$	- 1.19	6.4
10.	$\text{N}\equiv\text{CCH}_2\text{CH}=\text{CH}_2$	- 1.31	6.3
11.	$\text{HOCH}_2\text{CH}=\text{CH}_2$	- 1.49	6.0
12.	$\text{MeCO}_2\text{CMe}=\text{CH}_2$	- 1.51	6.1
13.	$\text{C}_6\text{H}_5\text{CH}_2\text{CH}=\text{CH}_2$	- 1.66	< 5.7
14.	$\text{Me}_3\text{CCH}=\text{CH}_2$	- 1.73	< 5.7
15.	$\text{EtOCH}=\text{CH}_2$	- 2.24	< 5.7
16.	$\text{MeOCMe}=\text{CH}_2$	- 2.48	< 5.7

^a From reference 68 unless otherwise noted. ^b Not available. Value is

based on theoretical calculations (see text). ^c From reference 66.

Figure 17 - $\text{Log} (k_{\text{add}}^{\text{Et}_3\text{N} \rightarrow \text{BH}_2^{\bullet}} / \text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1})$ vs. EA/eV . The numbers beside the points correspond to the olefins indicated in Table 10. The least squares line is drawn through the filled circles only. The open circles have been excluded for the reasons given in the text.

maintained below -1.5 eV (cf. olefins 13 to 16). A straight line through the points (filled circles) for olefins 4-12 yields gives $a = 9.0$ and $b = 2.0$, according to equation 34. The data points (open circles in Figure 17) for $\text{C}_6\text{F}_5\text{CH}=\text{CH}_2$ (1), $(\text{C}_6\text{H}_5)_2\text{C}=\text{CH}_2$ (2) and $\text{C}_6\text{H}_5\text{CMe}=\text{CH}_2$ (3) have been ignored for the "twisted" geometric reason previously mentioned, plus, for olefins 1 and 2, because their $k_{\text{add}}^{\text{Et}_3\text{N}\rightarrow\text{BH}_2^\bullet}$ values are likely to be limited by diffusion rather than by their EAs.

4.7.3 Nucleophilic comparison of $\text{Et}_3\text{N}\rightarrow\text{BH}_2^\bullet$

The values of a and b for the four nucleophilic carbon-centred radicals, studied by Fischer and coworkers⁶⁴⁻⁶⁸, and $\text{Et}_3\text{N}\rightarrow\text{BH}_2^\bullet$ are given in Table 11. It seems that as the radical becomes more nucleophilic both a and b increase. This is to be expected *when polar factors dominate reactivity*,⁶⁴⁻⁶⁸ i.e., when the activation energies are significantly lowered because the transition state is stabilized by its strong polar character.

It has been found that there is, in fact, a remarkably good linear correlation between a and b for the four carbon-centred radicals (plotted as filled circles in Figure 18). The a and b values for the $\text{Et}_3\text{N}\rightarrow\text{BH}_2^\bullet$ radical are given as a filled triangle. It lies close to the line defined by the correlation found for the four nucleophilic carbon-centred radicals studied by Fischer and co-workers. This demonstrates that $\text{Et}_3\text{N}\rightarrow\text{BH}_2^\bullet$ is much more nucleophilic than all four of the carbon-centered radicals.

Table 11. Parameters which describe, via equation 34, the kinetics of addition of nucleophilic radicals to mono- and 1,1-di-substituted olefins in terms of the olefins' electron affinities.

Radical	<i>a</i>	<i>b</i>	Reference
$\text{PhCH}_2^\bullet$	3.36	1.14	52, 53
$\text{HOCH}_2^\bullet$	5.57	1.53	48
$\text{Me}_3\text{C}^\bullet$	6.0	1.6	54
$\text{HOC}^\bullet\text{Me}_2$	6.46	1.71	47
$\text{Et}_3\text{N} \rightarrow \text{BH}_2^\bullet$	9.0	2.0	this work
$(\text{CH}_3)^\bullet$	5.78	0.97	56) ^a

^a The *a* and *b* values for $\text{CH}_3^\bullet$ do not lie on the line shown in Figure 15 for the other five radicals. The "anomalous" behaviour of the methyl radical has been attributed to its low nucleophilicity combined with its very high reactivity.

Figure 18 - The correlation between a and b (see equation 34 and Table 11).

4.8 Hydrogen Atom Abstraction from Electron-Deficient C-H Groups

The limited kinetic data for hydrogen abstraction from electron deficient C-H groups by $\text{Et}_3\text{N} \rightarrow \text{BH}_2^\bullet$ are consistent with relative rates measured by the ESR method for the "somewhat sterically crowded"¹² $\text{Me}_3\text{N} \rightarrow \text{B}^\bullet\text{H}\text{CMe}_2\text{CHMe}_2$ radical at a much lower temperature¹¹ (see last two columns of Table 5). This is rather surprising because the ratio of the rates of H-atom abstraction from $\text{H}_2\text{C}(\text{CO}_2\text{Et})_2 / \text{HC}(\text{CH}_3)(\text{CO}_2\text{Et})_2$ pair are largest (~20) for $\text{Me}_3\text{N} \rightarrow \text{B}^\bullet\text{H}\text{CMe}_2\text{CHMe}_2$ and decline as steric crowding about the radical center is reduced to a low of ~0.9 for $\text{Me}_3\text{N} \rightarrow \text{B}^\bullet\text{H}\text{Bu}^n$ ²⁰ ($\text{Et}_3\text{N} \rightarrow \text{BH}_2^\bullet$ was not examined). Therefore, it is doubtful whether the absolute $\text{Et}_3\text{N} \rightarrow \text{BH}_2^\bullet$ kinetic data, from this work, should be combined with the $\text{Me}_3\text{N} \rightarrow \text{B}^\bullet\text{H}\text{CMe}_2\text{CHMe}_2$ relative rates to derive even rough absolute rate constants for hydrogen atom abstraction from the less reactive substrates, such as $(\text{CH}_2\text{CO}_2\text{Et})_2$.

4.9 Final Remarks

The results reported herein highlight once again the important role played by polar factors in influencing the rates of homolytic reactions between uncharged species. This was demonstrated by all the reactions of $\text{Et}_3\text{N} \rightarrow \text{BH}_2^\bullet$ (addition to olefins, Cl and H atom abstractions), as well as through the partial influence on the kinetic solvent effects of the

generation of $\text{Et}_3\text{N}\rightarrow\text{BH}_2^\bullet$. It was also found that $\text{Et}_3\text{N}\rightarrow\text{BH}_2^\bullet$ is an extremely nucleophilic radical.

However, the triethylamine $\rightarrow$ boryl radical has a fairly fast β -scission and it is due to this instability that the triethylamine $\rightarrow$ borane complex will have a limited synthetic utility. This utility could be increased by using an amine $\rightarrow$ borane complex (example shown below) with a more stable amine $\rightarrow$ boryl radical.

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