Hydrogen Atom Transfer to Alkenes from Aminyl–Borane Radicals

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The aminyl–borane radical $Me\dot{N}H{\rightarrow}BH_3$, an isoelectronic nitrogen–boron bonded counterpart of the isopropyl radical, readily transfers a β-hydrogen atom from boron to simple alkenes to form alkyl radicals.

Homolytic addition of alkyl radicals to alkenes is well established and of considerable importance.[1,2] An alternative mode of reaction, namely transfer of a β-hydrogen atom from the alkyl radical to the C=C bond, has not been demonstrated experimentally for simple alkenes, although some evidence has been found for H-atom transfer from the cyclohexyl radical to dimethyl fumarate at elevated temperatures (≥520 K).[3]

The relative rates of addition and β-H-atom transfer reflect the thermodynamics of the two processes. For example, addition of the isopropyl radical to propene [equation (1a)] is exothermic by *ca.* 94 kJ mol^{-1},[4,5] whilst the degenerate H-atom transfer [equation (1b)] is, of course, thermoneutral.

The methylamine–boryl ($MeNH_2{\rightarrow}\dot{B}H_2$) (**1**) and methylaminyl–borane ($MeNH{\rightarrow}BH_3$) (**2**) radicals are isoelectronic counterparts of the n-propyl and isopropyl radicals, respectively. Whilst $MeCH_2\dot{C}H_2$ and $Me_2\dot{C}H$ are more stable than $MeCH{=}CH_2 + H^{\bullet}$ by 138 and 145 kJ mol^{-1}, respectively,[4,5] *ab initio* M.O. calculations predict $Me\dot{N}H{\rightarrow}BH_3$ to be more stable than $MeNH{\rightleftarrows}BH_2 + H^{\bullet}$ by only 7 kJ mol^{-1} and $MeNH_2{\rightarrow}\dot{B}H_2$ to be less stable than these cleavage products

$$Me_2\dot{C}H + MeCH{=}CH_2 \rightarrow Me_2CHCH_2\dot{C}HMe \quad (1a)$$

$$Me_2\dot{C}H + MeCH{=}CH_2 \rightarrow MeCH{=}CH_2 + Me_2\dot{C}H \quad (1b)$$

by 25 kJ mol^{-1}.† These results suggest that amine–boryl and aminyl–borane radicals might transfer a β-H-atom to alkenes much more readily than do alkyl radicals and here we show that (**2**) is indeed highly reactive in this regard.

We have found previously[8] that the reaction between photochemically generated t-butoxyl radicals and dimethylamine–borane leads initially to the amine–boryl radical $Me_2NH{\rightarrow}\dot{B}H_2$, but that this reacts rapidly with the parent amine–borane to yield the more stable isomeric aminyl–borane radical $Me_2\dot{N}{\rightarrow}BH_3$. Similarly, when a solution containing methylamine–borane[9] (1.0—1.5 M) and di-t-butyl peroxide (DTBP; 20% v/v) in Bu^tOH–Pe^tOH (Pe^t = t-pentyl) (3 : 1 v/v) was u.v. irradiated in the microwave cavity of an e.s.r. spectrometer, the spectrum of the methylaminyl–borane radical (**2**) was observed [*a*(3 B*H*) 63.9, *a*(3 C*H*) 24.1, *a*(N*H*) 19.4, *a*(^{14}N) 15.4, *a*(^{11}B) 13.3 G, and *g* 2.0036]. All the results described here were obtained at 282 ± 1 K, unless noted otherwise. On the basis of evidence analogous to that reported previously,[8] we propose that (**2**) is the product of thermodynamic control and is generated as shown in equations (2) and (3) from the initially formed amine–boryl radical (**1**).

$$Bu^tO^{\cdot} + MeNH_2{\rightarrow}BH_3 \longrightarrow \underset{(1)}{MeNH_2{\rightarrow}\dot{B}H_2} + Bu^tOH \quad (2)$$

$$MeNH_2{\rightarrow}\dot{B}H_2 + MeNH_2{\rightarrow}BH_3 \longrightarrow MeNH_2{\rightarrow}BH_3 + \underset{(2)}{Me\dot{N}H{\rightarrow}BH_3} \quad (3)$$

When the experiment was repeated in the presence of propene, the spectrum of (**2**) was replaced by that of the isopropyl radical to an extent which increased with the concentration of alkene (0.1—0.5 M). With propene concentrations above *ca.* 0.6 M, the aminyl–borane was no longer detectable, see Figure 1. Even under very forcing instrumental conditions, it was not possible to detect with certainty the spectrum of the n-propyl radical and the value of [$Pr^{i\cdot}$]/[$Pr^{n\cdot}$] must be >30. A wide variety of other alkenes can be reduced to alkyl radicals under similar conditions, the more stable radical product being formed with high regioselectivity when two isomers are possible. For example, $Me_2C{=}CH_2$, $Me_2C{=}CHMe$, and $Me_2C{=}CMe_2$ yield $Bu^{t\cdot}$, $Pe^{t\cdot}$, and $HCMe_2\dot{C}Me_2$, respectively; none of the less stable regioisomer was detectable from either of the first two alkenes. Competitive reduction of pairs of alkenes, making the usual assumptions to relate stationary state radical concentrations to their relative rates of formation,[10] showed that the ease of reduction increased along the series $MeCH{=}CH_2$ (1.0) < $Me_2C{=}CH_2$ (3.4) < $Me_2C{=}CMe_2$ (4.7). Selective removal of alkyl radicals by addition to the alkenes[11] was unimportant under these conditions, since relative radical concentrations depended only on the relative concentrations of the alkenes and not on their total concentration. The rate coefficients for addition of free hydrogen atoms to these alkenes in the gas phase at 298 K are in the order $MeCH{=}CH_2$ (1.0) ≃ $Me_2C{=}CMe_2$ (0.8) < $Me_2C{=}CH_2$ (2.5).[12]

U.v. irradiation of samples containing $MeNH_2{\rightarrow}BD_3$, DTBP, and $Me_2C{=}CMe_2$ in either Bu^tOH–Pe^tOH (3 : 1 v/v) or in aprotic 2,2,5,5-tetramethyltetrahydrofuran–oxirane (5 : 1 v/v) afforded the e.s.r. spectrum of $DCMe_2\dot{C}Me_2$, although $HCMe_2\dot{C}Me_2$ was also detectable. However, the relative concentration of the protiated radical increased, initially very rapidly, with the duration of photolysis and extrapolation indicated that $DCMe_2\dot{C}Me_2$ was the only product at zero irradiation time. These results show that it is the electrophilic aminyl–borane (**2**) which is the active reducing agent [*e.g.* equation (4)] and that the isomeric amine–boryl radical (**1**) is not involved, at least at *ca.* 282 K when the amine–borane concentration is >*ca.* 0.5 M.‡ Protium exchange into the BD_3 group evidently takes place during photolysis and the high rate of protium incorporation suggests that reaction (3) may be reversible to some degree under the experimental conditions, thus providing a chain mechanism for H/D-exchange.

$$Me\dot{N}H{\rightarrow}BH_3 + MeCH{=}CH_2 \xrightarrow{k_4} MeNH{\rightleftarrows}BH_2 + Me_2CH \quad (4)$$

$$Me\dot{N}H{\rightarrow}BH_3 \rightleftharpoons MeNH{\rightleftarrows}BH_2 + H^{\cdot} \quad (5)$$

It might be proposed that the reducing agent could be a free hydrogen atom formed by β-scission of (**2**), but to account for the progressive quenching of the spectrum of (**2**) as the concentration of propene is increased, *vide supra*, this would seem to require the existence of an equilibrium (5). Even though the monomeric aminoborane $MeNH{\rightleftarrows}BH_2$ is unstable with respect to its cyclic trimer, its concentration would be expected to build up to some extent during u.v. irradiation and thus, for a fixed concentration of propene, the stationary state value of [$Pr^{i\cdot}$]/[(**2**)] would decrease with photolysis time, which is contrary to observation. Moreover, the relative reactivities of alkenes towards the hydrogen atom,[12] albeit under different conditions, are significantly different from those towards the $MeNH_2{\rightarrow}BH_3$–$Bu^tO^{\cdot}$ couple.

The partial quenching of the spectrum of (**2**) which occurs with lower concentrations of propene permits the rate coefficient for H-atom transfer to be estimated.[13] For example, in Bu^tOH–Pe^tOH (3 : 1 v/v) the values of [$Pr^{i\cdot}$]/[(**2**)] and [$Pr^{i\cdot}$] were 0.22 and 1.7 × 10^{-7} M, respectively, when the propene concentration was 0.28 M. With the assumption[10] that the rate coefficients for self- and cross-reaction of the isopropyl radical are both 2.1 × 10^9 l mol^{-1} s^{-1},§ we estimate

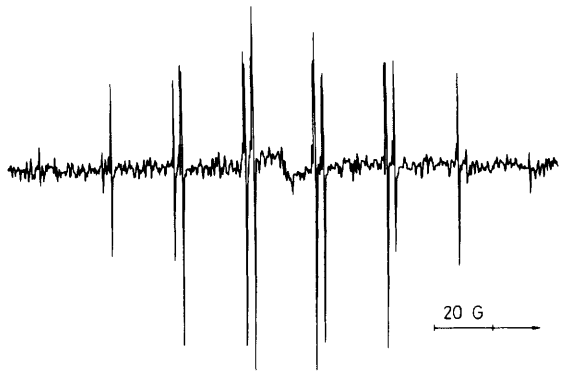

Figure 1. E.s.r. spectrum of the isopropyl radical obtained during u.v. irradiation of DTBP (20% v/v), $MeNH_2{\rightarrow}BH_3$ (1.2 M), and propene (1.4 M) in Bu^tOH–Pe^tOH (3 : 1 v/v) (G = 10^{-4} T).

† Calculations were performed using the GAUSSIAN 82 program package.[6,7] The energies of reaction at 0 K reported here (which should differ only slightly from ΔH°_{298}) refer to geometry optimised structures at the U(R)MP3(full)/6-31G**//U(R)HF/6-31G** level and include zero-point vibrational energy contributions scaled[7] by a factor of 0.9.

‡ The calculated vertical ionisation potentials of (**1**) and (**2**) are 6.5 and 10.8 eV, respectively.

§ This is the value of 2k_t for self-reaction of the isopropyl radical in 3-methylpentan-3-ol at 282 K, extrapolated from the data reported by Lipscher and Fischer.[14]

k_4 to be 1.6×10^3 l mol^{-1} s^{-1} at 282 K. Although (**2**) is calculated to be more stable than (**1**) by 32 kJ mol^{-1}, and thus β-H-atom transfer from the latter is more exothermic, (**1**) is rapidly converted into (**2**) in the presence of methylamine–borane. Not only is alkene reduction by (**2**) calculated to be highly exothermic [by 145 kJ mol^{-1} for reaction (4)], but it is also expected to be kinetically favoured because of the large unpaired electron population on the hydrogen atoms attached to boron. The value of a(3 BH) implies that when a B–H bond eclipses the nitrogen 2pπ-orbital, the spin population in the hydrogen 1s orbital will be *ca.* 25%. The aminyl–borane radical may thus be considered to be a 'carrier' of the hydrogen atom, and indeed it may be looked upon as a derivative of the perboryl radical $H_4B^{\bullet}$ in which one of the two strongly coupled protons has been replaced by an alkylamino group.[15] The aminyl–borane radicals derived from other primary amine–boranes react in a similar way to (**2**), but dimethylaminyl–borane $Me_2\dot{N}{\rightarrow}BH_3$ is a less reactive H-atom donor, as would be expected because of the appreciably smaller value[8] of a(3 BH) (46.4 G).

Preliminary e.s.r. experiments have also shown that β-H-atom transfer from (**2**) to arenes and dienes takes place readily under similar conditions. For example, 1,3,5-tri-t-butylbenzene affords a cyclohexadienyl radical [a(2 H) 41.6, a(2 H_{meta}) 2.65 G, and g 2.0027 at 304 K] by H-atom addition to an unsubstituted ring carbon atom. The conjugated diene 2,4-dimethylpenta-1,3-diene and the isomeric allene 2,4-dimethylpenta-2,3-diene both afford the 1,1,3,3-tetramethylallyl radical [a(6 H^1) 14.2, a(6 H^2) 13.0, a(1 H) 5.4 G, and g 2.0027 at 301 K].

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