PERKIN 2

Kinetics of the direct borane reduction of pinacolone in THF

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The kinetics of the borane reduction of the ketone pinacolone in THF depend strongly on the borane reagent. $NaBH_4$, which is present in commercial BH_3–THF as stabilizer, strongly catalyzes the reaction. The use of commercial BH_3–THF results in the borane reaction order of 1.6. In contrast, freshly prepared, pure BH_3–THF yields kinetics for which the main reaction, the reduction of the ketone by BH_3–THF forming the monoalkoxyborane, are first order in both reactants. Two further subsequent reactions have to be included in the reaction scheme in order to fit the kinetics by numerical integration. Results of semiempirical calculations are compared with experimental findings to eludicate the possible reaction mechanism of the main reaction.

Introduction

The enantioselective borane reduction of prochiral ketones catalyzed by chiral oxazaborolidines has aroused great interest because of its high synthetic utility.[1–4] Although a lot of information has already been gained about the mechanism of this reaction, considerable work is still to be done to find the optimum reaction conditions for high ee values. Certainly, one of the reasons for this unsatisfactory situation is the absence of significant kinetic studies. The actual catalytic cycle has to compete with the direct borane reduction of the ketone. Therefore, knowledge of the rate determining steps and the concentration and temperature dependences of the competing reactions is very important for a systematic optimization of the catalytic process. In this work we report our results of a kinetic study on the direct borane reduction of the ketone pinacolone (P) in tetrahydrofuran (THF).

Results and discussion

Reactivity of the borane solutions

Borane exists in THF as a 1 : 1 BH_3–THF (B–T) complex.[5,6] It has already been shown that the reaction of ketones with B–T in THF leads, *via* monoalkoxyborane intermediates, to the formation of dialkoxyboranes.[7,8] The subsequent hydrolysis of dialkoxyboranes can be used to produce the corresponding alcohols, as well as boric acid. The reaction of the ketone P with B–T was observed spectrophotometrically. The $n\pi^*$ absorption band of the ketone with a maximum extinction coefficient of $\varepsilon = 20$ dm^3 mol^{-1} cm^{-1} at 286 nm disappears completely during the course of reaction as is illustrated by the reaction spectra of Fig. 1. Since the absorbance of P decreases at the same rate throughout the entire region of the $n\pi^*$ band, it is evident that neither the intermediates nor products of the reaction contribute to the absorption in that wavelength range.

In our initial experiments we used commercial B–T solutions in THF as reducing agent. The reactivity of the reagent varied moderately from bottle to bottle, whereby Fluka and Aldrich reagents exhibited a similar reactivity. We observed a rather fast and strongly exothermic reaction with P. A mixture of overall concentrations of $[P]_o = 0.10$ mol dm^{-3} and $[B–T]_o = 0.46$ mol dm^{-3} reacts completely within 20 s leading to a temperature rise of 5.6 °C, which cannot be compensated in such a short time by the thermostat. Half of P is already reduced after 6 s (see Fig. 2). Since the reaction rate increases distinctly at the beginning, the reaction is autocatalytic. At 10% conversion of P the reaction rate has already reached twice its initial value. At this point of the reaction the temperature increase is estimated to be only 0.6 °C, which is clearly insufficient to explain the observed increase in the reaction rate.

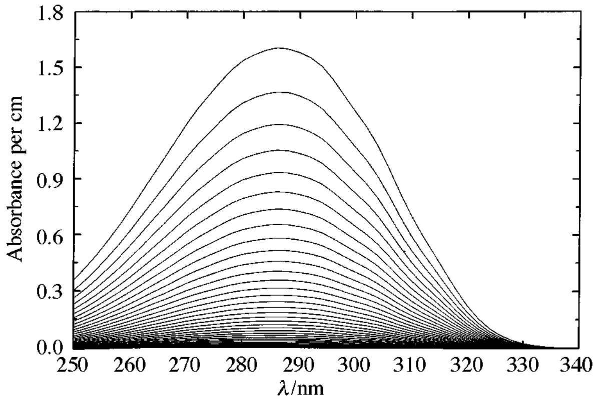

Fig. 1 Reaction spectra of the borane reduction of P ($[P]_o = 0.081$ mol dm^{-3}) for the overall concentration $[B–T]_o = 0.50$ mol dm^{-3} of freshly prepared B–T. The time interval between two consecutive spectra is 75 s.

The kinetic curves of the consumption of P can be compared with corresponding curves of the only kinetic study on the borane reduction of ketones published to date.[9] Klein and Dunkelblum presented manually drawn curves of the decrease of the ketone absorbance in the region of the $n\pi^*$ band for the reduction of the ketone dihydroisophorone by a large excess of B–T in THF. These curves lack the autocatalytic starting phase and are not monoexponential.[9] They determined the time for 50% conversion of the ketone (= half-lifetime $\tau_{\frac{1}{2}}$) for $[B–T]_o = 0.30$ mol dm^{-3} and a ketone concentration of 0.0125 mol dm^{-3} to be $\tau_{\frac{1}{2}} = 10$ s at 25 °C. We determined $\tau_{\frac{1}{2}} = 10$ s for the reaction of $[B–T]_o = 0.33$ mol dm^{-3} and $[P]_o = 0.08$ mol dm^{-3} at 20 °C. Thus, both ketones have a similar reactivity. Klein and Dunkelblum calculated from the first half-lifetime pseudo-first-order rate constants $k_{p1} = (\ln 2)/\tau_{\frac{1}{2}}$ by simplifying the kinetics with the assumption of monoexponential behaviour. A double logarithmic plot of k_{p1} *vs.* $[B–T]_o$ results in a linear correlation yielding the borane reaction order (RO) = 1.5 as slope.[9] If we proceed in the same way and estimate from our kinetic curves rate constants k_{p1} *via* values of $\tau_{\frac{1}{2}}$, we obtain the borane reaction order RO = 1.6. Thus, our experiments seem to confirm their results. However, the borane reaction order 1.5 in THF is quite surprising, since it requires, besides the essential monomeric borane species, the involvement of dimeric borane species in the reaction sequence. But species like B_2H_6 or B_2H_6–THF are only expected to play a negligible role in THF, as borane exists in THF as BH_3–THF complex.[5,6]

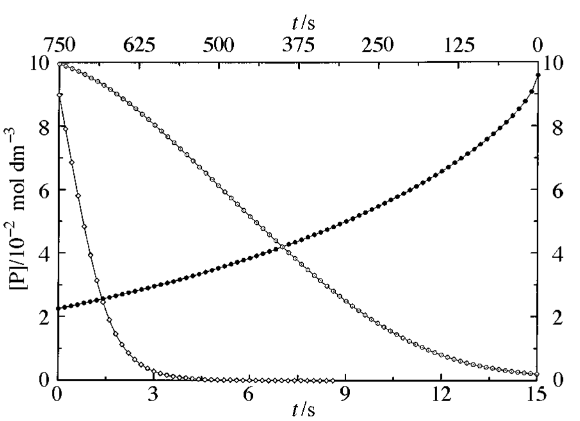

Fig. 2 Kinetic traces of the direct borane reduction of P with $[B–T]_o = 0.46$ mol dm^{-3}: (●) with freshly prepared B–T (upper timescale); (◇) with a freshly prepared B–T solution with $[NaBH_4]_o \approx 0.01$ mol dm^{-3} (lower timescale); and (⊙) with commercial B–T (Aldrich) (lower timescale)

In order to test whether the quality of the commercial B–T influences the kinetics of the borane reduction of ketones, we prepared fresh solutions of B–T in THF following the procedures described by Brown[10] or by Freeguard and Long.[11] To our surprise we observed much slower reactions and very different reduction kinetics if we used freshly prepared B–T solutions instead of the commercial B–T. However, we obtained similar results with the borane solutions prepared according to both different procedures, if these 'self-prepared' reagents were free of contamination by the reactants from which they had been prepared (BF_3–OEt_2, $NaBH_4$, I_2), which could act as catalysts. In fact, it has been shown that the addition of BF_3–OEt_2 catalyzes the borane reduction of ketones.[9,12,13] Since the reactivity of B–T was similar for products of both different synthetic procedures,[10,11] we may exclude the action of reaction inhibitors in the 'self-prepared' reagents as the cause of the changes in the reaction kinetics. Instead we must assume that the stabilizer and/or the decomposition products present in the commercially available B–T have catalyzing activity. Fig. 2 compares kinetic traces recorded for the reduction of P at the overall concentration $[B–T]_o = 0.46$ mol dm^{-3} by commercial (Aldrich) and by freshly prepared B–T. The half-lifetime of reaction $\tau_{\frac{1}{2}}$ increases by almost two orders of magnitude from 6 s for the commercial reagent to 330 s for the self-prepared B–T solution. After 6 weeks of storing the 'self-prepared' B–T solution at 4 °C in a refrigerator the $\tau_{\frac{1}{2}}$ decreased by about 30%. It is known that B–T decomposes slowly, with formation of boric acid butyl esters. Indeed, if boric acid tributyl ester (tributoxyborane, TBB) in a concentration of $[TBB]_o = 0.03$ mol dm^{-3} is added to a solution of $[P]_o = 0.10$ mol dm^{-3} and $[B–T]_o = 0.46$ mol dm^{-3}, a decrease in $\tau_{\frac{1}{2}}$ by a factor of three is observed, indicating that TBB has some catalyzing effect. The addition of small amounts of boric acid has almost no effect on the reaction. However, the addition of $NaBH_4$ changes the kinetics of the freshly prepared solutions drastically, as is illustrated in Fig. 2: $\tau_{\frac{1}{2}}$ is reduced to about 1 s for $[B–T]_o = 0.46$ mol dm^{-3} and $[NaBH_4]_o \approx 0.01$ mol dm^{-3}! Thus, it is clear that decomposition products of B–T and in principal $NaBH_4$, which is used as stabilizer in the commercial B–T, lead to a strongly enhanced reactivity. To our knowledge this is the first time that the catalyzing effect of $NaBH_4$ on the reduction of ketones by B–T has been documented.

The reactive species in the commercial B–T is still unknown. Since the reaction becomes so fast in the presence of $NaBH_4$ that it becomes impossible to hold constant the temperature of the reaction system, as required for quantitative evaluation of the kinetic experiments, we did not yet further investigate the influence of $NaBH_4$ on the borane reduction of ketone P. Without sufficient experimental data we are not yet in a position to speculate about the enhancing effect of $NaBH_4$ on the reaction.

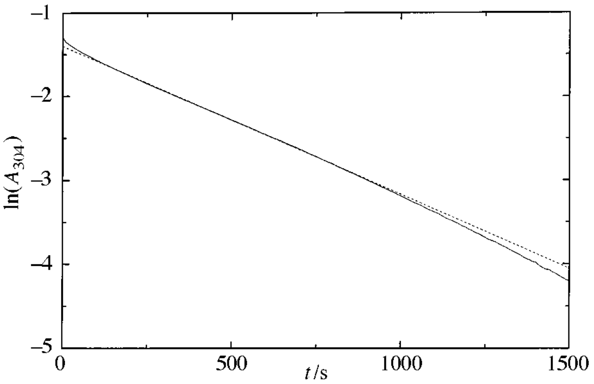

Fig. 3 Deviation of the reaction from monoexponential behaviour. A_{304} is the absorbance at 304 nm: $[P]_o = 0.10$ mol dm^{-3}; $[B–T]_o = 0.50$ mol dm^{-3}. (-----) Monoexponential behaviour, $k_{p1} = 0.0018$ s^{-1}, (——) experimental results.

To investigate the uncatalyzed borane reduction of P we used only 'self-prepared', fresh B–T solutions in further experiments. It should be noted that under the same experimental conditions the reactivity of the self-prepared B–T reagents still varied from preparation to preparation by about ±20%, independent of the method by which it was prepared.[10,11] The results presented here refer to the least reactive B–T preparations, assuming for these the absence of catalyzing contaminations.

Kinetics of the reduction

As illustrated by the semilogarithmic plot Fig. 3 for a fivefold excess of B–T, the principal part of the reduction of P can approximately be described by a monoexponential decay.

It is known from earlier investigations that two moles of ketone are reduced by one mole of B–T.[7,8] Therefore, the 5:1 excess of B–T corresponds to a 10:1 ratio of reducing equivalents and the main part of reaction is first order in P. The slope yields a main value for the overall pseudo-first-order rate constant at 20 °C of $k_{p1} = 0.0018$ s^{-1}. However, there are small but significant deviations from monoexponentiality. The slope of the experimental curve is steeper in the beginning of the reaction approaching the mean value after conversion of 10% P. The reason for this strange initial behaviour is not understood. After about 90% conversion of P the experimental slope increases again, indicating an acceleration of the reaction caused by the catalyzing effect of the produced monoalkoxyboranes, *vide supra*. The deviations of the experimental kinetic curves from monoexponentiality shown in Fig. 3 are typical and were found in all experiments.

In order to determine the reaction order in B–T two sets of reactions with constant $[P]_o$ but varying $[B–T]_o$ were performed. Overall pseudo-first-order rate constants k_{p1} were determined as described above. For low excess of B–T only the first $\frac{2}{3}$ of the reaction was used for the evaluation of k_{p1}. The double logarithmic plot of k_{p1} *vs.* $[B–T]_o$ is given in Fig. 4. A linear correlation of the data with slope 1.06 results, demonstrating that the main reaction of the reduction of P is first order in B–T. Here, we notice a second marked difference between the reaction kinetics observed with commercial and with freshly prepared B–T: the catalytic activity of the stabilizer $NaBH_4$ and of decomposition products present in the commercial B–T causes the reaction order in borane to vary from 1 to about 1.5. Obviously, the mechanism of the borane reduction and therefore the reaction rate changes distinctly. We suppose that the investigation of Klein and Dunkelblum (RO = 1.5) was also influenced by these effects.[9]

To interpret the kinetics of the consumption of P we have also to consider the results of product distribution studies. It has been shown by Brown and Rao[7] and by Pasto and Lepeska[8] that dialkoxyboranes are the principal reaction products formed in the borane reduction of ketones. Since no

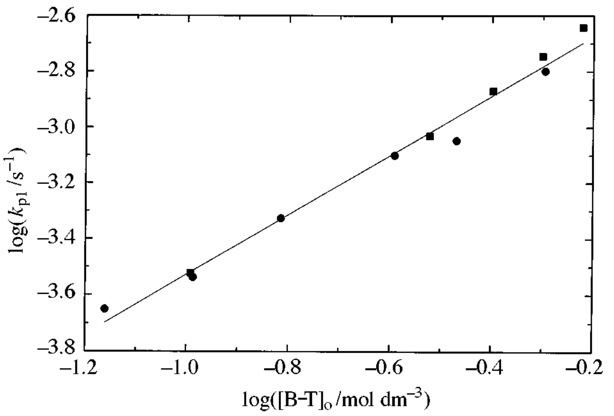

Fig. 4 Determination of the B–T reaction order: (■) $[P]_o = 0.10$ mol dm^{-3}; (●) $[P]_o = 0.12$ mol dm^{-3}; (——) fit: RO = 1.06

monoalkoxyborane (M) is observed, it was concluded that M is rapidly removed by reaction with ketone and/or with M to yield dialkoxyborane (D).[8,10] Trialkoxyborane and borane are produced in a much slower redistribution reaction of dialkoxyboranes,[8,14] due to the increasing steric demand of this reaction. If the alkoxy group is *tert*-butoxy, the equilibrium is reached at 25 °C in THF only after more than one month.[14] Therefore, the redistribution of D [= bis(2-*tert*-butylethoxy)borane] can be ignored on the short timescale of the reaction of P. It is assumed that, in a similar manner to B–T, monoalkoxyborane and dialkoxyborane form the 1 : 1 molecular complexes M–T and D–T in THF. Thus, besides reaction (R1), which leads to

$$\text{B–T} + \text{P} \longrightarrow \text{M–T} \quad k_1 \tag{R1}$$

the formation of M–T, two further reactions removing the intermediate M–T have to be considered. The initial product M–T reacts with P to form D–T in the subsequent reaction (R2).

$$\text{M–T} + \text{P} \longrightarrow \text{D–T} \quad k_2 \tag{R2}$$

M–T is also consumed by the redistribution reaction (R3)

$$2\,\text{M–T} \longrightarrow \text{D–T} + \text{B–T} \quad k_3 \tag{R3}$$

forming B–T and D–T. Reaction (R2) represents an autocatalytic branch of the overall reaction. k_1, k_2 and k_3 are the respective second-order rate constants.

Eqns. (1) to (4) hold for the reaction rates of reactants,

$$d[\text{B–T}]/dt = -k_1[\text{B–T}][\text{P}] + k_3[\text{M–T}]^2 \tag{1}$$

$$d[\text{P}]/dt = -k_1[\text{B–T}][\text{P}] - k_2[\text{M–T}][\text{P}] \tag{2}$$

$$d[\text{M–T}]/dt = k_1[\text{B–T}][\text{P}] - k_2[\text{M–T}][\text{P}] - 2k_3[\text{M–T}]^2 \tag{3}$$

$$d[\text{D–T}]/dt = k_2[\text{M–T}][\text{P}] + k_3[\text{M–T}]^2 \tag{4}$$

intermediate and product, whereby [I] represents the actual concentration of species I at reaction time t.

We have performed kinetic experiments on the borane reduction of P in the concentration ranges $0.04 \leqslant [\text{P}]_o \leqslant 1.40$ mol dm^{-3} and $0.062 \leqslant [\text{B–T}]_o \leqslant 0.56$ mol dm^{-3}. Solutions containing B–T in THF were mixed with solutions of P in THF. The respective overall concentrations in the reaction mixtures are $[\text{B–T}]_o$ and $[\text{P}]_o$. Since the molar concentration $[\text{T}] = 12.3$ mol dm^{-3} of pure liquid THF is much larger than $[\text{B–T}]_o$, [T] is set constant. The balance equations relating the known concentrations $[\text{B–T}]_o$ and $[\text{P}]_o$ with the actual concentrations of the four different species derived from borane and pinacolone, are given by eqns. (5) and (6).

$$[\text{B–T}]_o = [\text{B–T}] + [\text{M–T}] + [\text{D–T}] \tag{5}$$

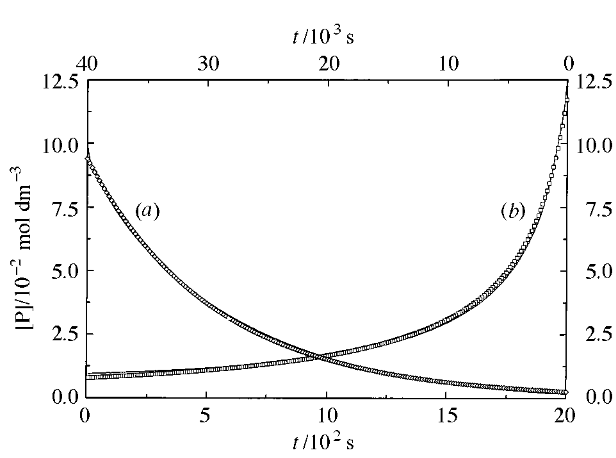

Fig. 5 Experimental and calculated kinetic curves. Concentrations in mol dm^{-3}, rate constants in dm^3 mol^{-1} s^{-1}. (*a*) $[\text{B–T}]_o = 0.51$; $k_1 = 0.0036$, $k_2 = 0.004$, $k_3 = 0.1$; lower timescale; (◇) calculated, (—) experimental data: (*b*) $[\text{B–T}]_o = 0.062$; $k_1 = 0.004$, $k_2 = 0.003$, $k_3 = 0.1$; upper timescale; (□) calculated, (—) experimental data.

$$[\text{P}]_o = [\text{P}] + [\text{M–T}] + 2[\text{D–T}] \tag{6}$$

The following initial concentrations hold true at $t = 0$: $[\text{M–T}]_i = 0$, $[\text{D–T}]_i = 0$, $[\text{B–T}]_i = [\text{B–T}]_o$ and $[\text{P}]_i = [\text{P}]_o$. The actual concentration of pinacolone is known at any time t. The kinetics could definitely be resolved, as experiments have been performed in dependence of both $[\text{P}]_o$ and $[\text{B–T}]_o$. The system of differential equations (1) to (4) was solved by numerical integration considering the known initial concentrations and eqns. (5) and (6). The fit parameters k_1, k_2 and k_3 were varied until the calculated decay of [P] matched the experimental decay. The whole set of experimental kinetic curves can be reproduced on the basis of the reactions (R1) to (R3) by the following constants: $k_1 = 0.0037 \pm 0.0006$ dm^3 mol^{-1} s^{-1}, $k_2 = 0.003 \pm 0.001$ dm^3 mol^{-1} s^{-1} and $k_3 = 0.2 \pm 0.1$ dm^3 mol^{-1} s^{-1}. Fig. 5 shows the results of the numerical integration for reactions with a large excess and a very small excess of reducing agent. Both reactions are well fitted with practically the same rate constants.

The pseudo-first-order rate constant k_{p1} of the overall reaction depends linearly on $[\text{B–T}]_o$, see also Fig. 4. A mean value of $k_{p1}/[\text{B–T}]_o = 0.0033 \pm 0.0005$ dm^3 mol^{-1} s^{-1} was obtained for the overall reaction in a large number of experiments. It is only for the reaction (R1) of the above kinetic scheme that the reaction rate of P is directly proportional to [B–T]. Therefore, it is clearly this reaction which is the most important for the overall reduction of P in the presence of an excess of B–T. The autocatalytic reaction (R2) is less important, although M–T reduces P with a similar rate constant as does B–T. The finding that k_2 is only little smaller than k_1 seems reasonable, since both reactions (R1) and (R2) are very similar and differ only by one substituent of the reducing agent. The redistribution reaction (R3) is the least important, despite its large rate constant. This is a consequence of the low concentration of the intermediate M–T.

Temperature dependent kinetic experiments on the reduction of P have been performed in the presence of an excess of B–T in the range 10.0 to 29.2 °C. Reaction (R1) dominates the overall reduction under these conditions. Therefore, the resulting activation parameters $\Delta G^‡ = 93.4 \pm 0.4$ kJ mol^{-1}, $\Delta H^‡ = 52 \pm 6$ kJ mol^{-1} and $\Delta S^‡ = -0.14 \pm 0.02$ kJ mol^{-1} K^{-1} apply to the reaction B–T + P ⟶ M–T.

Mechanistic considerations

The equilibrium $B_2H_6 + 2\,\text{THF} \rightleftharpoons 2\,BH_3\text{–THF}$ lies far to the right side in THF.[5,6] It has already been suggested that the complex B–T is the reactive species in the hydroboration reaction of alkenes in THF.[15] We assume that this holds also true for the reaction with ketones. From the systematic studies of Brown and co-workers[7,16,17] on the reduction of organic compounds by borane it is known that a distinct graduation in reactivity of the substrates exists. The reactivity of aldehydes and ketones increases strongly with increasing electron density at the oxygen atom of the carbonyl group in diglyme and in THF. Thus, B–T acts as Lewis acid in these reactions.

Considering reaction (R1), it seems reasonable that the oxygen of the ketone P couples to the boron atom of the B–T complex during the formation of the pinacolone–borane adduct in THF. A complex P–B–T with a five-fold-coordinated boron atom would appear to be a highly improbable intermediate. We therefore assume that the first step (R1.1) of reaction (R1) is the

$$\mathrm{B{-}T} + \mathrm{P} \longrightarrow \mathrm{P{-}B} + \mathrm{T} \quad \Delta H_{1.1} = -11 \qquad (\mathrm{R}1.1)$$

nucleophilic substitution of T in B–T by P forming P–B with a four-fold-coordinated boron atom. The second step (R1.2) is

$$\mathrm{P{-}B} \longrightarrow \mathrm{M} \quad \Delta H_{1.2} = -137 \qquad (\mathrm{R}1.2)$$

the subsequent hydride shift yielding the monoalkoxyborane M with a three-fold-coordinated boron, which again adds THF in the third step (R1.3) to compensate its electron deficit and to

$$\mathrm{M} + \mathrm{T} \longrightarrow \mathrm{M{-}T} \quad \Delta H_{1.3} = -27 \qquad (\mathrm{R}1.3)$$

yield M–T. It is possible that the latter two steps might also occur simultaneously as step (R1.4).

$$\mathrm{P{-}B} + \mathrm{T} \longrightarrow \mathrm{M{-}T} \quad \Delta H_{1.4} = -164 \qquad (\mathrm{R}1.4)$$

We have performed semiempirical calculations using the AM1 parametrization[18] to see whether the results support such a mechanism for the formation of M–T = 2-*tert*-butylethoxyborane–THF from P and B–T. The following heats of formation (kJ $\mathrm{mol^{-1}}$), have been obtained: B–T (−200.4), P (−258.3), P–B (−224.3), T (−245.1), M (−361.5) and M–T (−633.5). With these results we obtain for the possible steps i of reaction (R1) the reaction enthalpies ($\Delta H_{1.i}$ in kJ $\mathrm{mol^{-1}}$) given above. These values, however, should only be given qualitative significance.

Of course, reaction enthalpies are not directly related to rate constants. Nevertheless, they can be used as very approximate guidelines in a kinetic discussion. The least exothermic step is the nucleophilic substitution of T in B–T by P. The experimental finding that reaction (R1) is first order in both B–T and P actually points to step (R1.1) as the rate determining step of the reaction sequence. Step (R1.2), the hydride shift, is strongly exothermic, and one would expect this reaction step to be rather fast. Complexation of M with T [step (R1.3)] is calculated to be moderately exothermic. Since step (R1.4) is only little more exothermic than step (R1.2) it would appear that the hydride shift occurs already in the adduct P–B without the supporting participation of T, as assumed in step (R1.4). Thus, the results of the semiempirical calculations suggest that the sequence of steps (R1.1) to (R1.3) is the most plausible mechanism of reaction (R1). The complexation of D by T is also calculated to be exothermic (−12 kJ $\mathrm{mol^{-1}}$), a similar value to that for the complexation of M by T, supporting the assumption that the differently substituted boranes form complexes with THF in THF solution.

Conclusions

It has been found that the kinetics of the borane reduction of P in THF depend strongly on the borane reagent. Decomposition products and principally the stabilizer $\mathrm{NaBH_4}$ present in the commercially available B–T product lead to a drastic acceleration of the reaction and to a change in the reaction mechanism. In contrast to the commercial B–T, freshly prepared pure B–T is much less reactive. Comparison of the results of semiempirical calculations with experimental findings suggest that the principal reaction, the formation of the monoalkoxyborane from ketone and B–T, proceeds as a sequence of three reaction steps. Our results indicate that the first step, the nucleophilic substitution of T in the complex B–T by the ketone P, is probably rate determining.

Experimental

Kinetic measurements

A computerized Hewlett-Packard HP8452A diode array spectrophotometer allowing 0.2 s as the shortest time interval between two consecutive spectra was used. $\mathrm{O_2}$-free, self-prepared B–T solutions were transparent above 230 nm. Commercial 1 mol $\mathrm{dm^{-3}}$ solutions of B–T had absorption bands at 272 and 278 nm with maximum absorbance of 1.0 per cm at 278 nm, which remained unchanged during reaction. Unless otherwise stated, all kinetic experiments were carried out at 20 °C. Since THF is a very aggressive solvent, the RX 1000 stopped flow accessory from Applied Photophysics (optical path 0.2 or 1 cm) was modified as follows. (1) All pasted connections between tubes were replaced by steel/Teflon couplings or screwed connections made of Kel-F. (2) Drain tube equipped Teflon tubes were connected directly to the inlet and outlet valves so that sample solutions could be fed under Ar directly from the Schlenk-flasks into the stopped flow syringes. (3) The stop syringe was removed and the outlet valve was connected *via* a Teflon tube with a bottle which was open to the atmosphere so that gas bubbles developing in the reaction solution could not build up pressure, which might otherwise press the solution through the cell during measurement leading to a baseline shift. (4) The flow was stopped by means of an adjustable rod which moved in parallel to the pistons of the reagent syringes until it struck a microswitch triggering the diode array spectrophotometer.

Reagents

Pinacolone (P, 2,2-dimethylbutan-3-one) (Aldrich, 98%) was dried over $\mathrm{K_2CO_3}$ and distilled in an Ar-atmosphere into Schlenk-flasks containing 4 Å molecular sieves. THF (Riedel-de-Haën, +99.9%, stabilized with 2,6-di-*tert*-butyl-4-methylphenol) was dried over Na–K pearls and distilled under Ar. $\mathrm{NaBH_4}$ (Aldrich, 98%) and $\mathrm{BF_3{-}OEt_2}$ (Aldrich) were used as received. B–T was either purchased (Aldrich, 1 mol $\mathrm{dm^{-3}}$ in THF, stabilized with <0.005 mol $\mathrm{dm^{-3}}$ $\mathrm{NaBH_4}$), (Fluka, purum, 1 mol $\mathrm{dm^{-3}}$ in THF, UV spectrum identical with the Aldrich reagent) or synthesized according to Brown (from $\mathrm{BF_3{-}OEt_2}$ and $\mathrm{NaBH_4}$)[10] or Freeguard and Long (from $\mathrm{NaBH_4}$ and $\mathrm{I_2}$),[11] respectively. The B–T content of the solutions was determined at regular intervals by gas volumetry.[19] Hereby it was found that the actual concentrations of the commercial B–T solutions were only about 90% of the nominal concentrations. Presumably the difference had already decomposed. The handling of the materials and the preparation of the solutions was carried out under Ar to avoid contamination by water.

Acknowledgements

Financial support by the Bundesministerium für Bildung, Wissenschaft, Forschung und Technologie, grant no. 03D0029B3 and by the Fonds der Chemischen Industrie is gratefully acknowledged.

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Paper 7/03698A
Received 28*th May* 1997
Accepted 27*th August* 1997