

using a fast-flow, quenching kinetic apparatus. The borane-THF solution and TME-THF solution (containing an inert internal standard for glpc analysis) are rapidly mixed in a reaction cell consisting of a four-jet tangential mixing chamber (operating under turbulent flow conditions) and tubular reaction chamber which then feeds into a second four-jet, tangential mixing chamber in which the quenching reagent (triethylamine or Dabco) is rapidly mixed with the reacting solution.⁴³ The entire cell and tubular reaction chamber are con-

structed of Teflon and are immersed in a constant temperature bath. The reagent solutions are transferred to jacketed 50-ml syringes (maintained at the same temperature as the constant temperature bath) which are driven by a Servo-Tek precision-speed (0.1% rpm reproducibility) variable-rpm motor. The time constants for the reaction cell and the tubular reactors were measured by accurately determining the volume of the cell and the tubular reactor and the volume flow per unit time at a given drive speed (motor rpm).

The quenched reaction mixtures were analyzed for the amount of unreacted TME by glpc.

(43) The reaction cell is modeled after that designed by W. R. Ruby (*Rev. Sci. Instrum.*, **26**, 460 (1955)). The authors gratefully acknowledge

Eastman Kodak Co. and Drs. W. R. Ruby and C. A. Bishop for providing design blueprints and technical advice.

Measurement of the Relative Rate Ratios of the First and Second Steps of the Hydroboration Reaction and the Rates of Alkylborane Redistribution Reactions. Discussion of the Overall Mechanism of the Hydroboration Reaction^{1,2}

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Abstract: The relative rates of the first and second steps of the hydroboration reaction of alkenes capable of proceeding to the di- and trialkylborane stage have been measured. In all cases studied the rate constant for formation of the dialkylborane from monoalkylborane and alkene is larger than the rate constant for the formation of alkylborane from borane and alkene. The rate constants for the redistribution reactions $\text{BH}_3 + \text{R}_3\text{B} \rightleftharpoons \text{R}_2\text{BH} + \text{RBH}_2$, $2\text{RBH}_2 \rightleftharpoons \text{R}_2\text{BH} + \text{BH}_3$, and $2\text{R}_2\text{BH} \rightleftharpoons \text{R}_3\text{B} + \text{RBH}_2$ have been determined at 40° for the *n*-propylborane system ($\text{R} = n\text{-C}_3\text{H}_7$). All of the bimolecular rate constants for the forward and reverse redistribution reactions are considerably smaller than the hydroboration reaction rate constants. The formation of dialkylborane from monoalkylborane and alkene in systems in which alkylborane monomer-dimer equilibrium constants are not prohibitively large is proposed to occur *via* reaction between an alkylborane monomer-tetrahydrofuran complex and alkene. The greater reactivity of the monoalkylborane relative to borane is attributed to a weaker complexing interaction in the monoalkylborane-tetrahydrofuran complex than in the borane-tetrahydrofuran complex, thus resulting in a lowering of the activation energy for nucleophilic attack by an alkene on borane-tetrahydrofuran with partial displacement of the tetrahydrofuran. The differing stereochemical results obtained in the hydroboration of alkenes with monoisopinocampheylborane under various conditions are discussed in terms of the relative rates of addition *vs.* redistribution reactions. It is concluded that hydroboration with monoisopinocampheylborane produces alcohol of one configuration, whereas hydroboration with diisopinocampheylborane produces alcohol of opposite configuration. The results and conclusions reported in this article reinforce the conclusion that the hydroboration of an alkene with borane in tetrahydrofuran involves the direct reaction between a molecule of the borane-tetrahydrofuran complex and a molecule of the alkene.

In the previous article we discussed the possible mechanisms for the hydroboration of alkenes with borane and substituted boranes, and presented kinetic and thermodynamic data for the hydroboration of tetramethylethylene (TME) with borane in tetrahydrofuran (THF), as well as ¹H/³H and ¹⁰B/¹¹B kinetic isotope data for the hydroboration of other alkenes with borane and alkylboranes.³ It was reported that the hydroboration of TME with borane in THF is first order in both TME and borane. From an analysis and comparison of rates and activation parameters

for various possible mechanisms it was concluded that the hydroboration of alkenes with both borane and monochloroborane⁴ occurs by nucleophilic attack by alkene on a borane-THF complex in a rather early transition state involving a concerted, syn addition of B-H to the double bond, as proposed earlier.⁵

In the present paper we wish to present kinetic data pertaining to the formation of di- and trialkylboranes under hydroboration conditions in THF (eq 1-3), alkylborane-borane redistribution reactions (eq 4-6), and equilibrium constant data on alkylborane monomer-dimer equilibria (eq 7-11). (In eq 2 and 3 reaction may occur either *via* the alkylborane monomer ($n = 1$) or the alkylborane dimer ($n = 2$). Competi-

(1) Part XXV of a series of Transfer Reactions Involving Boron; for part XXIV, see D. J. Pasto, B. Lepeska, and T.-C. Cheng, *J. Amer. Chem. Soc.*, **94**, 6083 (1972).

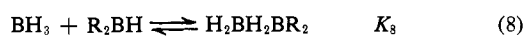
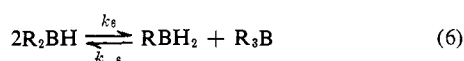
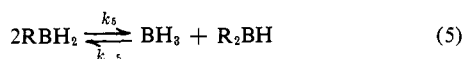
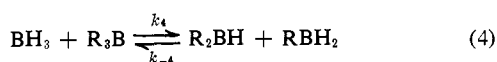
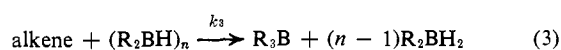
(2) Acknowledgment is made to the donors of the Petroleum Research Fund administered by the American Chemical Society for partial support of this research (Grant No. 1225, A1,3), and to the National Institutes of Health for partial support (Grant No. CA 07194).

(3) See ref 1.

(4) D. J. Pasto and S.-Z. Kang, *J. Amer. Chem. Soc.*, **90**, 3797 (1969).

(5) H. C. Brown and G. Zweifel, *ibid.*, **81**, 247 (1959).

tion between these two alternatives will be discussed later in this article.)



Results

Determination of the Relative Rates of Formation of Mono- and Dialkylboranes in the Hydroboration of Alkenes. Solutions of borane and alkene in THF were rapidly mixed in molar ratios of 1.0:0.3 and 1.0:1.0 and were allowed to stir for 2–5 min (under these reaction conditions the alkene is consumed and the product distribution is still under kinetic control). An excess of anhydrous methanol was then added to the reaction mixture and, after the evolution of hydrogen ceased (~5 min), the reaction mixtures were concentrated by distillation and were analyzed by ^{11}B nmr spectroscopy to determine the borinate:boronate product ratios. A computer program was written to simulate the formation of mono- and dialkylboranes (RBH_2 and R_2BH) in consecutive second-order reactions (eq 1 and 2) from the starting borane:alkene ratios to the final $\text{RBH}_2:\text{R}_2\text{BH}$ product ratios at 98% consumption of the alkene. The rate constant for the formation of RBH_2 , k_1 in eq 1, was arbitrarily assigned a value of 1.00, while values of k_2 for the formation of R_2BH in eq 2 were initially set at slightly higher values. The computer program calculated the $\text{RBH}_2:\text{R}_2\text{BH}$ integrated product ratio to 98% consumption of the alkene, and then compared the calculated $\text{RBH}_2:\text{R}_2\text{BH}$ ratio with the experimentally observed ratio. Depending on the comparison of the calculated and experimental product ratios, the value of k_2 was appropriately modified until the calculated and experimental ratios agreed to within 2%.⁶ The calculated values

(6) A number of assumptions are involved in these calculations. The first assumption is that the formation of R_2BH is first order in both alkene and RBH_2 . This assumption is in contrast to the report by Brown and Moerikofer that the reaction of bis-3-methyl-2-butylborane (disiamylborane, BMBB) is first order in BMBB dimer.^{7,8} The validity of the assumption in the present study will be discussed in detail in the Discussion of this paper. Further assumptions are made in ignoring the effect of monomer-dimer equilibria (eq 7–11) on the effective concentration of monomeric borane and monoalkylborane. Ignoring the monomer-dimer equilibria will result in the calculation of a value of k_2 which is smaller than its real value because the concentration of the monomeric monoalkylborane is less than the total concentration of monoalkylborane in solution as used in the calculations (*i.e.*, k_2 as calculated is the product of the real k_2 and the equilibrium constants for the appropriate monomer-dimer equilibria). Despite the assumptions made in these calculations, the values of k_2 calculated from the different initial reactant ratios agree reasonably well, although a

of k_2 relative to a value of unity for k_1 are given in Table I.

Table I. Calculated Values of k_2 (Eq 2) Relative to a Value of Unity for k_1 (Eq 1)^a

Alkene	k_2	
	$\text{BH}_3:\text{alkene}$ 1.0:0.3	ratio 1.0:1.0
Styrene	3.4	1.4
1-Hexene	4.3	1.9
2-Ethyl-1-hexene	3.0	2.3
<i>trans</i> -3-Hexene	3.8	3.1
3-Methyl-2-butene	2.8	2.0

^a Experiments run under kinetically controlled product distribution conditions.

Measurement of $^1\text{H}/^3\text{H}$ Isotope Effects for Dialkyl- and Trialkylborane Formation. The $^1\text{H}/^3\text{H}$ isotope effects for the hydroboration of alkenes with mono- and dialkylboranes were determined using the procedures outlined in the previous article.¹ In these reactions an excess of the appropriate alkene, except in the case of 1,5-cyclooctadiene, was added to the [^3H]borane solution to form the desired mono- or dialkylborane. After an elapsed period of time sufficient to guarantee completion of the formation of the mono- or dialkylborane, a weighed quantity of the second alkene was added. In the case of 1,5-cyclooctadiene, the 9-borabicyclononane was prepared from 1,5-cyclooctadiene and [^3H]borane and purified as described by Knights and Brown.⁹ Weighed quantities of 9-borabicyclononane- ^3H and alkene were then dissolved in THF and allowed to react. After completion of the addition reaction (30 min at 25°) the reaction mixtures were subjected to oxidation, and the excess initial alkene and the two alcohol products were isolated by preparative glpc. The tritium content of the recovered alkene and the two alcohol products was determined in the usual manner. The available [^3H]borane in the mono- and dialkylboranes was calculated by subtracting the tritium content appearing in the recovered alkene and in the alcohol derived from the initial alkene from the total tritium content in the original [^3H]borane. The isotope effects were then calculated as described previously¹ (see Table II).

Table II. Hydrogen-Tritium Isotope Effects for the Hydroboration of Alkenes with Mono- and Dialkylboranes^a

Alkene	Alkylborane	$^1\text{H}/^3\text{H}_3$
1-Hexene	Bis-3-methyl-2-butylborane	4.75
1-Hexene	Diisopinocampheylborane	3.99
1-Butene	Diisopinocampheylborane	2.88
1-Hexene	Dicyclohexylborane	2.34
1-Hexene	9-Borabicyclononane	1.49
1-Decene	2,3-Dimethyl-2-butylborane	6.68 ^b (6.17) ^c
2-Octene	2,3-Dimethyl-2-butylborane	6.84 ^b (6.32) ^c
2-Methyl-2-butene	2,3-Dimethyl-2-butylborane	1.98

^a Alkene-alkylborane ratio of 1.0:0.3. ^b Calculated on the basis of no exchange. ^c Calculated on the basis of complete exchange.

consistent trend is noted between the values derived from the data with initial reactant ratios of 1.0:0.3 and 1.0:1.0.

(7) H. C. Brown and A. W. Moerikofer, *J. Amer. Chem. Soc.*, **83**, 3417 (1961).

(8) H. C. Brown and A. W. Moerikofer, *ibid.*, **85**, 2063 (1963).

(9) E. F. Knights and H. C. Brown, *ibid.*, **90**, 5280 (1968).

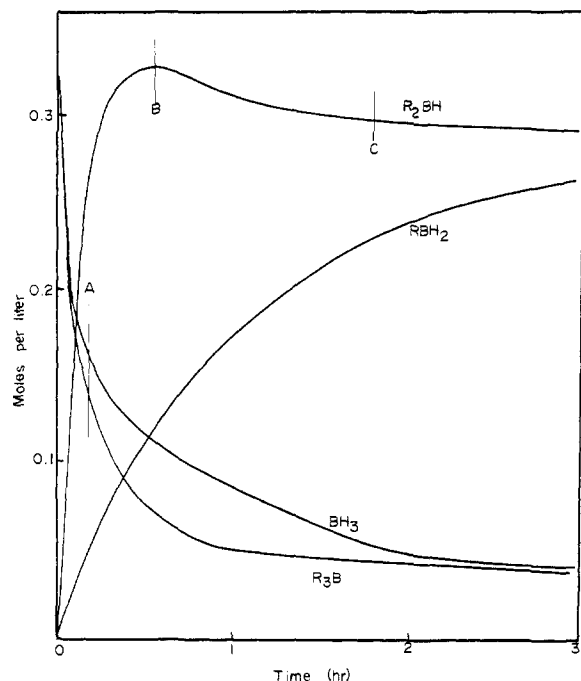


Figure 1. Redistribution of tri-*n*-propylboron with borane in tetrahydrofuran at 40°.

The recovered excess α -pinene and cyclohexene contained considerable tritium, indicating reversibility in the formation of the dialkylborane, or in an alkene displacement reaction in the hydroboration of the second alkene with the dialkylborane.¹⁰ The excess 2-methyl- and 2,3-dimethyl-2-butene recovered in these experiments contained only trace quantities of tritium.

Kinetics of the Redistribution Reactions (Eq 4–6). Solutions of tri-*n*-propylboron and triisopropylboron in THF were mixed with solutions of borane in THF in mole ratios of 1.0:0.5 and 1.0:1.0 and thermostated at 25 and 40°. Aliquots were periodically removed and quenched with an excess of *cis*-2-butene dissolved in THF. (The rate of hydroboration of the various alkylborane species was shown to be considerably faster than the redistribution reactions in a control experiment.) The quenched reaction mixtures were analyzed by glpc to determine the relative amounts of R_3B , $R_2R'B$, $RR_2'B$, and $R_3'B$ ($R = n$ - or isopropyl; $R' = 2$ -butyl). Negligible rearrangement (<1%) of isopropyl to *n*-propyl, or *vice versa*, was observed as indicated by glpc analysis of the trialkylboron mixtures and by basic hydrogen peroxide oxidation and glpc analysis of the product alcohol mixtures. Plots of concentration of species *vs.* time for the *n*-propyl system at 40° are shown in Figure 1.¹¹

Values for the redistribution equilibrium constants (eq 4–6) and the monomer–dimer equilibrium constants (eq 7–11) were determined by integration of the ¹¹B nmr spectra of equilibrium mixtures employing

(10) H. C. Brown, N. R. Ayyangar, and G. Zweifel, *J. Amer. Chem. Soc.*, **86**, 1071 (1964).

(11) An unusual feature is evident in the plots of the concentration of species *vs.* time data for the *n*-propylborane system at 40°. The concentrations of the species undergo damped oscillations as equilibrium is approached. This phenomenon was quantitatively reproducible from experiment to experiment. Such behavior might be expected to occur in complex, multiple-reaction chemical systems.¹²

(12) I. Prigogine and R. Lefever, *J. Chem. Phys.*, **48**, 1695 (1968).

proton heteronuclear decoupling followed by analysis of the data by computer techniques¹³ (see Tables III

Table III. Redistribution Equilibrium Constants (Eq 4–6)¹³

Eq	—R = <i>n</i> -propyl—		—R = isopropyl—	
	25°	40°	25°	40°
4	82 ^a (31) ^b	63 (20)	189 (165)	840 (160)
5	0.098 (0.33)	0.12 (0.43)	0.87 (1.65)	0.47 (1.4)
6	0.13 (0.10)	0.13 (0.12)	0.60 (0.04)	0.23 (0.02)

^a Calculated on the basis of total alkylborane concentration (monomer plus dimer). ^b Calculated on the basis of alkylborane monomer concentration.

Table IV. Monomer–Dimer Equilibrium Constants (Eq 7–11)

Eq	R = <i>n</i> -propyl		R = isopropyl	
	25°	40°	25°	40°
7	0.6	0.95	0.6	0.95
8	0.8	2.4	3.2	6.3
9	1.0	1.6	1.8	2.4
10	1.4	2.8	1.8	2.4
11	2.3	3.8	20	25

and IV). The factors involved in determining the value of these equilibrium constants have been discussed.¹³

An attempt was made to calculate the redistribution reaction rate constants from a reaction scheme comprising eq 4–11, employing computer techniques designed for use with multiple equilibrium systems. Unfortunately, either the reaction system was too complex for the minimization routine employed in the computer program, and/or the equilibrium constants determined for eq 4–11 were not sufficiently internally consistent and accurate to allow the computation to converge. Fortunately, however, data from portions of the *n*-propylborane–borane redistribution concentration *vs.* time plots could be subjected to analytical solutions to derive values for the rate constants k_4 , k_5 , and k_6 .

At the onset of reaction the only species present in solution are trialkylborane and borane. Both species exist exclusively as monomers in THF solution, *i.e.*, no hydrogen-bridged dimers of R_3B with BH_3 and BH_3 with BH_3 can be detected by ¹¹B nmr spectroscopy. Borane exists as a rapidly exchanging complex (on the nmr time scale) with the solvent THF, whereas R_3B does not complex with THF as indicated by a lack of change in the chemical shift of the α hydrogens of THF in solutions of R_3B in THF.¹⁴ As at the very onset of the reaction the only reaction proceeding is that of R_3B with BH_3 (eq 4), k_4 can be determined directly by solution of the second-order rate expressions for the disappearance of R_3B and BH_3 . The second-order plots for these functions are nicely linear out to the time indicated by line A in Figure 1, and gave the same values for k_4 within experimental error. The estimated accuracy in the determination of k_4 is $\pm 10\%$.

The second-order plot for the disappearance of BH_3 displays a discontinuity followed by a second linear portion (see Figure 2). The change in the slope is due to the incurrence of the redistribution reaction of mono-

(13) D. J. Pasto, V. Balasubramanian, and P. W. Wojtkowski, *Inorg. Chem.*, **8**, 594 (1969).

(14) D. J. Pasto and P. Balasubramanian, *J. Amer. Chem. Soc.*, **89**, 295 (1967).

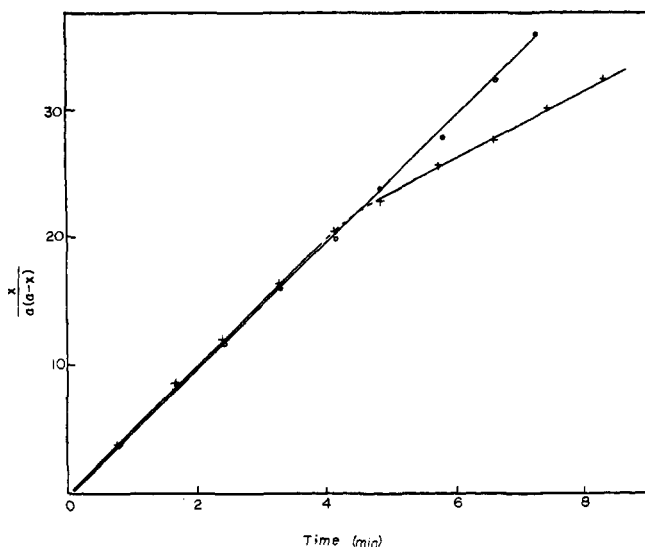


Figure 2. Second-order kinetic plots for the disappearance of tri-*n*-propylboron (O) and borane (+).

alkylborane producing BH_3 (eq 5). The value of k_5 was calculated in the second linear portion in the following manner. The excess concentration of BH_3 over that being consumed in reaction 4 and the deficiency in the concentration of RBH_2 compared to that formed in reaction 4 were calculated and then the value of k_5 was determined using normal procedures. As a check on the accuracy of the calculations, the concentration of R_2BH being formed in reactions 4 and 5 was calculated using the values of k_4 and k_5 calculated above and was compared with the experimental R_2BH concentration at early reaction times, the values agreeing to within 10%.

The value of k_6 was determined from the second-order plot for the disappearance of R_2BH between points B and C in Figure 1. The value of k_6 is sufficiently less than the other rate constants in the system such that at point B the rate-controlling reaction in the approach toward equilibrium is eq 6; *i.e.*, it is assumed that the net rate of formation and consumption of R_2BH in eq 4 and 5 is zero. The second-order plot for the disappearance of R_2BH between points B and C of Figure 1 is reasonably linear (Figure 3). The accuracy in the determination of k_6 is certainly considerably less than for the determination of k_4 or k_5 , and may be as large as $\pm 100\%$. Despite the relatively large uncertainty in the value of k_6 , k_6 is obviously less than k_4 and k_5 , and, as we shall see in the Discussion, is less than any of the hydroboration rate constants k_1 , k_2 , and k_3 for the hydroboration of a terminal monosubstituted alkene.

Values for k_{-4} , k_{-5} , and k_{-6} were calculated from the values of k_4 , k_5 , and k_6 and the redistribution equilibrium constants for monomeric species (the parenthesized values in Table III) for the reactions 4, 5, and 6. The rate constants are given in Table V.

The redistribution data for the tri-*n*-propylboron-borane system at 25° do not allow as distinct a kinetic analysis as do the data for 40°, and the rate constants calculated as outlined above, except for k_4 , are undoubtedly associated with larger uncertainties. The redistribution data for the triisopropylborane-borane system are even less easy to analyze in terms of the in-

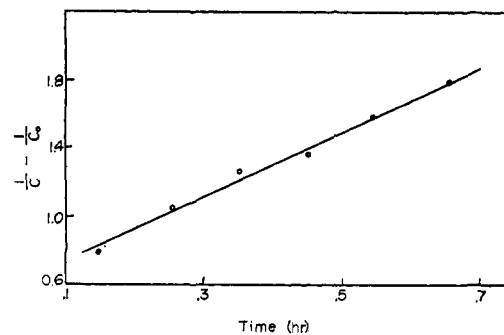


Figure 3. Second-order kinetic plot for the disappearance of di-*n*-propylboron in the B \rightarrow C region of Figure 1.

Table V. Second-Order Rate Constants ($\text{l. mol}^{-1} \text{sec}^{-1}$) for Alkylborane Redistribution Reactions (Eq 4-6)^a

Rate constant	R = <i>n</i> -propyl		R = isopropyl	
	25°	40°	25°	40°
k_4	0.86	4.97	6.9×10^{-3}	3.5×10^{-2}
k_{-4}	0.027	0.25	4.2×10^{-3}	2.2×10^{-4}
k_5	2.6	18.4		
k_{-5}	26.3	156		
k_6		0.0031		
k_{-6}		0.0073		

^a Rate constants for which no value is given could not be derived from the available data.

dividual rate constants. Values for k_4 at 25 and 40° are estimated from the data derived at very short reaction times. These rate constants are approximately one-hundredth the values of k_4 for the *n*-propylboron-borane system. From the total time required to attain equilibrium in the isopropyl system relative to the *n*-propyl system, all of the rate constants in eq 4-6 must be considerably smaller in the isopropyl system. The rate constants for eq 4-6 are given in Table V.

Qualitative redistribution rate data have been derived for a few alkylborane systems under typical hydroboration conditions. The alkene was subjected to hydroboration (alkene-borane ratio of 1:1) in THF at 25° and aliquots were periodically removed and quenched with methanol. The quenched reaction mixtures were concentrated and the RBH_2 - R_2BH product ratios determined by integration of the alkane borinate and boronate peaks in the ^{11}B nmr spectra. Unfortunately, the ^{11}B nmr line widths derived with some systems, in particular with the isopinocampheyl system, were too broad to allow for a quantitative analysis of the RBH_2 - R_2BH product ratios. The qualitative redistribution rate data are presented in Table VI.

Table VI. Qualitative Redistribution Rate Data Derived under Typical Hydroboration Conditions at 25°

Alkene	R_2BH - RBH_2 ratios at time after completion of hydroboration reaction (hr)			
	0.5	1.0	12	23
1-Hexene	2.4	0.98	0.78	0.57
Styrene	1.5	1.4	0.64	0.51
Propenylbenzene	0.88	0.82	0.60	0.56
3-Methyl-2-butene	2.3		0.91	0.67

Discussion

Mechanism of Formation of Dialkylborane. The reaction of borane with an alkene, capable of leading to

the formation of a di- or trialkylborane, in a 1.0:0.3 or a 1.0:1.0 mole ratio under kinetically controlled conditions, leads to the formation of a mixture of RBH_2 and R_2BH in which the $\text{R}_2\text{BH-RBH}_2$ ratio is greater than unity¹⁵ (see Table VI). This observation is at first somewhat surprising in view of the observation by Fehlner¹⁷ that the gas-phase reaction $\text{C}_2\text{H}_5\text{BH}_2 + \text{CH}_2=\text{CH}_2 \rightarrow (\text{C}_2\text{H}_5)_2\text{BH}$ proceeds approximately 20 times slower than the gas-phase reaction $\text{BH}_3 + \text{CH}_2=\text{CH}_2 \rightarrow \text{C}_2\text{H}_5\text{BH}_2$.

There are two possible pathways for the formation of R_2BH in the hydroboration of an alkene in THF solution. One pathway involves two consecutive addition steps, eq 1 and 2, while the other pathway involves the rapid disproportionation (redistribution) of RBH_2 according to eq 5. These two processes can be easily distinguished by comparison of the rate constants involved in the two reaction pathways. The rates for the redistribution reactions (eq 4-6) have been determined for $\text{R} = n$ -propyl and inferred from the redistribution data for $\text{R} =$ isopropyl (see Table IV). The specific rate constant for the hydroboration of TME with BH_3 in THF at 25° has been determined to be $1.48 \text{ M}^{-1} \text{ sec}^{-1}$. The specific rate constants for the hydroboration of mono-, di-, and trisubstituted alkenes fall in the range 10^2 - $1 \text{ M}^{-1} \text{ sec}^{-1}$ as estimated from the relative reactivities of alkenes reported by Brown and Moerikofer⁵ and the specific rate constant for the hydroboration of TME. Values of k_2 in eq 2 relative to an arbitrarily assigned value of k_1 of 1.0 in eq 1 range from approximately 1.4 to 4.3, or in terms of specific rate constants from about 2 to $6 \text{ M}^{-1} \text{ sec}^{-1}$. The rate constants for the disproportionation of RBH_2 are approximately one-hundredth the value of k_2 . Therefore, the dialkylboranes are formed via consecutive addition reactions in which $k_2 > k_1$, and not via the disproportionation of the dialkylboranes.

The trends in the reaction rates illustrated in Table I for eq 2 relative to eq 1 are readily rationalized in terms of changes in the degree of solvent complexation with BH_3 and RBH_2 , and hydrogen-bridged dimer formation. Physical data indicate that BH_3 in THF exists only in the monomeric form, and that the BH_3 is complexed with THF.¹⁸ In the preceding article it was proposed that hydroboration in THF involves the direct reaction of a molecule of the $\text{BH}_3 \cdot \text{THF}$ complex with a molecule of the alkene. The effect of alkyl substitution on boron on the monomer-dimer equilibrium constants for eq 7-11 (see Table IV) has been discussed in terms of a balance between the steric effects in the alkylborane-THF complexes and in the hydrogen-bridged dimers, the steric effects being more severe in the THF complexes because of the shorter distances between the alkyl group(s) on boron and the α -methylene groups of the THF ligand relative to the distances between the terminal hydrogens and/or alkyl groups in the hydrogen-bridged dimers. As the number and size of the alkyl groups on boron increases, the alkylborane-THF complex decreases in stability, thus favoring the formation of the hydrogen-bridged dimers.

(15) This has been observed previously in qualitative studies on the hydroboration of 1-pentene and cyclopentene carried out by Brown and coworkers.¹⁶

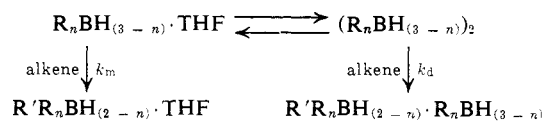
(16) H. C. Brown, A. Tsukamoto, and D. B. Bigley, *J. Amer. Chem. Soc.*, **83**, 4703 (1960).

(17) T. P. Fehlner, *ibid.*, **93**, 6366 (1971).

(18) See the discussion and references in reference of footnote 1.

The sensitive balance between THF complex formation relative to hydrogen-bridged dimer formation manifests itself in two ways on the rate of the second step of the hydroboration reaction (illustrated in Scheme I). As the reaction of diborane with alkenes in the

Scheme I



gas phase is considerably slower than the reaction of borane with ethylene in the gas phase,¹⁷ and bis-3-methyl-2-butylborane dimer⁵ reacts 10^{-2} - 10^{-4} the rate of reaction of monomeric borane with alkenes in THF, it can safely be concluded that hydrogen-bridged dimeric species are considerably less reactive in the hydroboration reaction than are the monomeric, solvent-complexed species (*i.e.*, $k_d \ll k_m$ in Scheme I). In systems in which the monomer-dimer equilibrium constants are relatively small, a considerable quantity of the monoalkylborane exists in the monomeric form complexed with THF, and one therefore concludes that in such systems it is the monomeric form of the alkylborane which reacts with alkene to form the more highly alkyl-substituted borane. Although the steric effects increase in the order $\text{BH}_3 < \text{RBH}_2 < \text{R}_2\text{BH}$, which would lead to a decrease in reactivity in the same order toward addition to an alkene, the stabilities of the THF complexes decrease in the order $\text{BH}_3 \cdot \text{THF} > \text{RBH}_2 \cdot \text{THF} > \text{R}_2\text{BH} \cdot \text{THF}$ due to the steric effects, thus leading to an increase in reactivity in the order given. Thus the steric effect of an alkyl group on boron produces opposing effects on the reactivity of borane and alkylboranes toward the hydroboration of an alkene.

The introduction of an alkyl group on boron also introduces an electronic effect which must be considered. Due to the greater electronegativity of carbon (2.5) relative to boron (2.0), the replacement of hydrogen (2.1) on boron by an alkyl group leads to an increase in the electropositive character of the boron atom. This trend is nicely illustrated by the results of extended Hückel calculations¹³ which are given in Table VII.

Table VII. Electron Densities Calculated by the Extended Hückel Method

Species	+ charge on B	- charge on H of B-H
BH_3	0.495	0.165
RBH_2^a	0.65	0.184
R_2BH^a	0.81	0.197
R_3B^a	0.98	

^a The values cited are for *n*-alkylboranes; *sec*-alkylboranes give ~ 0.02 higher positive charge densities on boron.

The increased electrophilic character of boron with increasing alkyl substitution will increase the tendency for both THF complexation and hydrogen-bridged dimer formation, as well as increase the reactivity of the alkylborane toward attack on a π -electron system relative to borane. The extended Hückel calculations also indicate that the partial negative charge on the hydrogen bonded to boron increases with increasing alkyl substitution. As the transition state for the hydroboration reaction involves the concerted formation

of both the C-H and C-B bonds, the increased electrophilic character of boron and the increased electro-negative character of the hydrogen should facilitate the addition reaction.

The observation that monomeric monoalkylboranes are more reactive than borane toward hydroboration in THF indicates that the increase in reactivity of the $\text{RBH}_2 \cdot \text{THF}$ complexes relative to $\text{BH}_3 \cdot \text{THF}$ and the electronic effects in the transition state outweigh the direct steric effects generated in the transition state between the alkyl group(s) on boron with the substituents on the double bond.

A different situation obtains in cases where the monomer-dimer equilibrium constants are very large. In these cases the monomer concentration is reduced to a level where product formation *via* hydroboration by the monomer is overcome by the formation of product by hydroboration involving the hydrogen-bridged dimer. Such is the case with bis-3-methyl-2-butylborane (disiamylborane)^{4,5} which exists essentially exclusively as the dimer in THF solution, and has been shown to react with alkenes in a reaction which is first order in BMBB dimer.

Trialkylborane Formation. The rate of formation of trialkylborane (R_3B) from R_2BH and alkene (eq 3) appears to be considerably faster than the rate of formation of R_3B by disproportionation of R_2BH (eq 6). In hydroboration reactions leading to the formation of trialkylboranes, the reactions generally proceed to completion in a time period shorter than would be required to form trialkylborane by the redistribution reaction in eq 6. In the experiments involving the determination of the $k_2:k_1$ ratios, only very small quantities of R_3B were ever formed. Qualitatively we can imply that $k_2 \gg k_3$.

The formation of trialkylborane can occur either by reaction of dialkylborane monomer with alkene (eq 6, $n = 1$), or a dialkylborane-containing hydrogen-bridged dimeric species (eq 6, $n = 2$, or $n = 2$ in Scheme I). The rate of formation of trialkylborane *via* hydroboration with dialkylborane monomer is expected to be considerably reduced owing to an increased tendency to form the hydrogen-bridged dimeric species. In contrast, the increased tendency for dimer formation is expected to result in increased trialkylborane formation *via* hydroboration with the dimeric species. Bis-3-methyl-2-butylborane (disiamylborane) is typical of a dialkylborane undergoing reaction *via* the dimer. The complexity of the reaction systems containing less sterically demanding alkyl functions (*i.e.*, primary alkylboranes) does not permit one to distinguish between the two possible modes of formation of trialkylborane illustrated in Scheme I ($n = 2$).

Transition State Structure for Formation of Di- and Trialkylboranes. The kinetic isotope effects presented in this and the previous article¹ decrease markedly with increasing substitution on both boron and on the double bond. All of the isotope effects are primary in nature, and are consistent with a rate-determining transition state involving a concerted, four-centered addition of B-H to the double bond. Even in the reactions involving the addition of alkylborane dimers to alkenes (see Table II), the hydrogen-tritium isotope effects are substantial and are characteristic of a primary isotope effect and are consistent with four-centered transition states.

Asymmetric Induction in Hydroboration. The hydroboration of alkenes with optically active organoboranes, derived by the hydroboration of an optically active alkene, followed by basic hydrogen peroxide oxidation, leads to the production of optically active alcohols. Several models have been proposed to account for the observed asymmetric induction;¹⁹⁻²² however, the results of the present study do not allow for distinction between the proposed models.

One aspect of the asymmetric hydroboration reactions is, however, interesting and merits comment. Brown and coworkers¹⁹ proposed a model to account for the observed configuration of the alcohols formed in the hydroboration of terminal, cis-disubstituted, and cyclic alkenes with diisopinocampheylborane (DPCB) dimer. However, in the hydroboration of trans-disubstituted and hindered alkenes with DPCB dimer, which occurs with the displacement of one molecule of α -pinene, the Brown model does not lead to the correct prediction of the configuration of the alcohol product.

Mislow and coworkers²³ observed that the immediate utilization of the reagent formed from α -pinene and borane in THF in a 1:1 mole ratio results in the formation of alcohol whose absolute configuration is in accord with the Brown model. However, if the reagent is allowed to stand at room temperature for a few hours before hydroboration of the second alkene, an alcohol of opposite configuration is obtained. Mislow proposed that the "initial 1:1 adduct of α -pinene with $\text{BH}_3 \cdot \text{THF}$ undergoes rearrangement and/or disproportionation on standing" and the "initial adduct is believed to be 1,1-diisopinocampheyl-diborane predominantly in equilibrium with tetraisopinocampheyl-diborane and borane."²³

The results presented and discussed in this article support a portion of Mislow's suggestions and further clarify these observations. The reaction of α -pinene with borane in THF in a 1:1 mole ratio initially produces a mixture of BH_3 , RBH_2 , and R_2BH which is rich in R_2BH (all species exist in the monomer-dimer equilibria illustrated in eq 7-11). Immediate use of this mixture results in a product derived by hydroboration of the three species in which asymmetric product is derived predominantly by hydroboration with R_2BH , or its dimer, producing alcohol of one net configuration. On standing, the R_2BH undergoes disproportionation, producing a reagent containing predominantly RBH_2 or its dimeric species. Hydroboration with this reagent leads to product formation predominantly with RBH_2 or its dimer, and must produce alcohol of opposite configuration. Similarly, in the hydroboration of terminal, cis-disubstituted, and cyclic alkenes with DPCB dimer, product is derived from hydroboration with R_2BH , or its dimer, giving alcohol of one configuration, whereas the hydroboration of trans-disubstituted and sterically hindered alkenes proceeds by initial elimination of one molecule of α -

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pinene from DPCB to produce an RBH_2 , or its dimer, which then reacts with alkene to ultimately produce alcohol of opposite configuration. It thus appears possible to be able to prepare either configurational isomer of an alcohol, or any other derivative derivable from an alkylborane, from a single optical isomer of

α -pinene by adjustment of the stoichiometry and mode of preparation of the asymmetric hydroboration reagent.

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Mono- and Diprotonation of *N*-Acylthioureas in Aqueous Sulfuric Acid

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Abstract: The basicities of *N*-acetylthiourea, *N*-benzoylthiourea, and eight substituted *N*-benzoylthioureas have been determined by a spectrophotometric method. Thiocarbonyl protonation takes place in 35–60% sulfuric acid and follows the H_0''' value of the solution; the Hammett ρ value for the protonation of meta- and para-substituted *N*-benzoylthioureas is -0.42 . A second protonation, on the amide oxygen, takes place in 65–96% sulfuric acid, and follows the H_A value of the solution; for this protonation ρ is -0.86 .

The protonation of amides (A) to their conjugate acids (AH^+) in aqueous sulfuric acid takes place on the carbonyl oxygen,^{2,3} and the ionization ratio ($I \equiv [\text{AH}^+]/[\text{A}]$) is found to depend on the acidity of the solution as measured by the H_A acidity function⁴

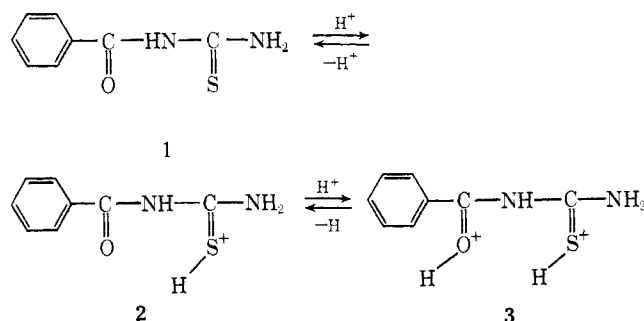
$$\log([\text{AH}^+]/[\text{A}]) = \text{p}K_{\text{AH}^+} - H_A \quad (1)$$

where K_{AH^+} ($\equiv -\text{antilog p}K_{\text{AH}^+} = a_{\text{H}} \cdot a_{\text{H}^+}/a_{\text{AH}^+}$) is the thermodynamic dissociation constant of the conjugate acid. The conjugate acid of benzamide has a $\text{p}K_{\text{AH}^+}$ of -1.74 , so that the amide is half-protonated in 35.2% sulfuric acid.⁴ On the other hand, the protonation of *N*-substituted thioureas (B) occurs on the thiocarbonyl sulfur atom^{2,5} and has been found^{6,7} to follow the H_0''' acidity function⁸

$$\log([\text{BH}^+]/[\text{B}]) = \text{p}K_{\text{BH}^+} - H_0''' \quad (2)$$

N-Methylthiourea has a $\text{p}K_{\text{BH}^+}$ of -1.75 , and is half-ionized in 22.6% sulfuric acid.⁷ Thus it is almost identical in basicity with benzamide, although it is half-protonated in less concentrated acid because its protonation is governed by a different acidity function.

In *N*-benzoylthiourea (1) both amide and thiourea functions may be expected to have reduced basicities, and it becomes of interest to consider the question: will protonation take place first on the thiourea sulfur or on the benzoyl oxygen?⁹ We show below that in this molecule both oxygen and sulfur sites have reduced but approximately equal basicities, but that because their protonation is governed by different acidity functions (H_A and H_0'''), sulfur is protonated first to give the conjugate acid 2, and then in stronger acid oxygen is protonated to give the conjugate acid 3.



Evidence from which we conclude that the first protonation, occurring in 35–60% sulfuric acid, takes place on the thiourea thiocarbonyl (rather than on the amide carbonyl) consists of three experimental findings. First, the changes in the ultraviolet absorption (see Table I) are qualitatively very similar to those observed when *N*-methylthiourea is protonated in sulfuric acid, and different from those observed when benzamide is protonated. This comparison is shown in Figure 1. For both *N*-methylthiourea and *N*-benzoylthiourea the strong absorption band at longer wavelength is most

(9) Protonation on nitrogen may be assumed to take place to a negligible extent for reasons discussed in ref 2. The experimental work described in the present paper can be interpreted without the necessity of invoking any appreciable N-protonation.

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(2) For a judicious survey of the early literature, see A. R. Katritzky and R. A. Y. Jones, *Chem. Ind. (London)*, 722 (1961); for important later references see R. J. Gillespie and J. Birchall, *Can. J. Chem.*, **41**, 148, 2642 (1963). M. Liler, *Chem. Commun.*, 115 (1971), while conceding that amides are predominantly O-protonated in concentrated acid solutions, argues that in dilute aqueous acids N-protonation becomes predominant because the N-protonated amide is more hydrated than the O-protonated amide. This last assertion lacks any experimental support; indeed, it would seem likely from the activity coefficient studies of Sweeting and Yates³ to be the reverse of the truth.

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