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Hydroboration Kinetics. 2.[1] Improved Procedure for Following the Kinetics for the Reaction of Alkenes with 9-Borabicyclo[3.3.1]nonane. Further Evidence for the Dissociation Mechanism

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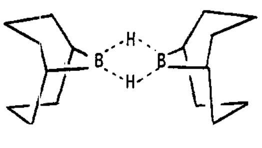
The kinetics of the hydroboration of alkenes with 9-borabicyclo[3.3.1]nonane dimer, $(9\text{-BBN})_2$, was studied by an improved procedure. The rate of the disappearance of the infrared absorption of the B–H–B bridges of $(9\text{-BBN})_2$ at 1570 cm^{-1} was followed by a quantitative infrared spectrometer. The kinetic data obtained by this improved procedure further confirmed the earlier conclusion that the hydroboration of alkenes with $(9\text{-BBN})_2$ proceeds through prior dissociation of the 9-BBN dimer into the monomer, followed by the reaction of the monomer with the alkenes. In addition, this infrared spectrophotometric procedure provides a convenient method for the study of kinetics and mechanisms of many other reactions of $(9\text{-BBN})_2$.

Since the discovery of the hydroboration reaction,[3] the chemistry of organoboranes has been rapidly explored.[4] Many fascinating characteristics have been discovered. However, the intimate details of the hydroboration mechanism are not yet understood. Several different reaction mechanisms have been proposed and much speculation has been published.[5]

The major problem in delineating the mechanism of hydroboration has been the paucity of kinetic data. The difficulty is that boranes are sensitive to both oxygen and water vapor in the atmosphere. Consequently, they must be handled under an inert atmosphere. Moreover, hydroboration with borane (BH_3) itself offers additional difficulties. The overall reaction with an alkene is very complex,[6] involving three consecutive addition reactions, three redistribution equilibria, and five monomer–dimer equilibria. In addition, the borane intermediates may form complexes with the ether solvents such as the $BH_3{\cdot}THF$ complex in THF solvent.[7]

Recently, we have circumvented these difficulties by the use of 9-borabicyclo[3.3.1]nonane (9-BBN) as the hydroborating agent.[1] 9-BBN exists exclusively as the dimer, $(9\text{-BBN})_2$, in certain solvents, such as CCl_4, cyclohexane, benzene, and diethyl ether. However, since it has only one reactive center per boron, the kinetics is much simpler. The remarkable thermal stability and the high purity of $(9\text{-BBN})_2$[8] make it an ideal dialkylborane dimer for kinetic studies.



The previous kinetic studies of the hydroboration of alkenes with $(9\text{-BBN})_2$ have clearly established that the reaction proceeds through prior dissociation of $(9\text{-BBN})_2$ into the monomer (eq 1), followed by the reaction of the

$$(9\text{-BBN})_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2(9\text{-BBN}) \qquad (1)$$

$$9\text{-BBN} + \text{alkene} \xrightarrow{k_2} B\text{-alkyl-9-BBN} \qquad (2)$$

monomer with the alkenes (eq 2). This is in sharp contrast with the earlier study of disiamylborane dimer, $(Sia_2BH)_2$,[9] where a direct reaction of $(Sia_2BH)_2$ with the alkenes was proposed (eq 3 and 4).

$$(Sia_2BH)_2 + \text{alkene} \rightarrow Sia_2BR + Sia_2BH \qquad (3)$$

$$Sia_2BH + \text{alkene} \xrightarrow{\text{fast}} Sia_2BR \qquad (4)$$

For clarification of this discrepancy and testing of the generality of the proposed dissociation mechanism with $(9\text{-BBN})_2$, it became evident that a systematic study of the reactions of $(9\text{-BBN})_2$ with various substrates such as alkynes, aldehydes, ketones, alcohols, and amines was necessary.[10]

However, before such a systematic study can be carried out, there is one technical difficulty to be overcome. The previous kinetic studies of hydroboration of alkenes with $(9\text{-BBN})_2$ were carried out by an indirect analytical technique. Aliquots of the reaction mixture were periodically withdrawn and quenched in an alcohol solution. The alcoholized samples were analyzed by GLC for residual olefin by using an internal standard technique. Although this method gives reliable data, it is tedious and very time consuming. The accuracy of the kinetic data suffers from the limited number of aliquots taken (usually ten) and the indirect nature of the analytical technique. Rapid reactions (those nearly complete in 10 min) are very difficult to study since their time scale approaches the rate of quenching with an alcohol and the rate at which aliquots can be withdrawn.

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Table I. Rate Data and Rate Constants for the Hydroboration of Cyclopentene (0.400 M) with $(9\text{-BBN})_2$ (0.200 M) in Carbon Tetrachloride at 25 °C

t, s	$[(9\text{-BBN})_2]$,[a] M	[cyclopentene], M	10^4k_1,[b] s^{-1}
0	0.200	0.400	
500	0.185	0.370	1.55
1000	0.173	0.346	1.46
3000	0.131	0.262	1.42
5000	0.096	0.191	1.48
7000	0.070	0.139	1.50
9000	0.050	0.100	1.54

[a] Calculated from eq 7. [b] Calculated from the equation $k_1t = \ln [b/(b - 2x)]$, where b is the initial concentration of cyclopentene and $b - 2x$ is the concentration at time t.

Table II. Effect of Concentrations on the Rate Constants for the Hydroboration of Cyclopentene, Cyclohexene, and *cis*-3-Hexene with $(9\text{-BBN})_2$ in Carbon Tetrachloride at 25 °C

init concn, M		10^4k_1, s^{-1}	$10^4k_{3/2}$, $M^{-1/2}\ s^{-1}$	10^4k_2,[b] $M^{-1}\ s^{-1}$
alkene	$(9\text{-BBN})_2$			
		Cyclopentene		
0.400	0.200	1.54	2.41	7.76
0.400	0.100	1.58	1.21	4.81
0.200	0.100	1.58	3.54	16.4
		Cyclohexene		
0.400	0.200	0.194	0.314	1.05
0.400	0.100	0.456	0.324	1.58
0.200	0.100	0.176	0.345	1.37
		cis-3-Hexene[a]		
0.400	0.200	1.07	1.69	5.52
0.400	0.100	1.45	1.08	4.75
0.200	0.100	0.925	2.07	9.49

[a] The kinetic data did not fit well to any of the integrated kinetic expressions. [b] The second-order rate constant.

Therefore, it became evident that the development of a direct analytical technique using a spectrometer was necessary. Since the ultraviolet spectrometer had already been widely applied to many quantitative kinetic studies, it was first considered. Unfortunately, it was soon discovered that $(9\text{-BBN})_2$ does not have any absorption in the ultraviolet region.

However, it was known that $(9\text{-BBN})_2$ exhibits a very strong infrared absorption at 1570 cm^{-1} due to the boron–hydrogen bridges.[8a] This suggested that a quantitative infrared spectrometer might be utilized to follow the reaction by monitoring the absorption at 1570 cm^{-1}. Indeed, this technique has been proven to be invaluable in various kinetic studies with $(9\text{-BBN})_2$.[10] It offers a convenient method of following the reaction rate continuously. All of the kinetic data are recorded when the reaction is over. No subsequent tedious GLC analyses are necessary. Since no quenching procedure is needed with this technique, it greatly minimizes the possibility of errors inherent in the indirect quenching method. In addition, a relatively fast reaction with a half-life of 1 min can be easily studied. The precision and reproducibility of the data are improved also.

This infrared technique was first applied to the kinetic study of hydroboration of alkenes with $(9\text{-BBN})_2$. Since the kinetics of hydroboration of alkenes with $(9\text{-BBN})_2$ had already been established by the quenching method, this study would serve as a check to this newly developed procedure. In addition, it would give further evidence for the proposed dissociation mechanism.

Results and Discussion

The kinetics of hydroboration with $(9\text{-BBN})_2$ was studied by addition of various alkenes to the solutions of $(9\text{-BBN})_2$ in the solvent maintained at 25 °C. The reaction mixtures were pumped through a sodium chloride infrared cell. The rates of the disappearance of the infrared absorption of the boron–hydrogen bridges of $(9\text{-BBN})_2$ at 1570 cm^{-1} were monitored by a quantitative infrared spectrometer. The absorbances were recorded on the chart paper of a recorder.

First-Order Kinetics. The hydroboration of cyclopentene with $(9\text{-BBN})_2$ in CCl_4 was found to follow first-order kinetics, first order in $(9\text{-BBN})_2$ only (eq 5), by the quenching method.

$$-d[(9\text{-BBN})_2]/dt = k_1[(9\text{-BBN})_2] \qquad (5)$$

With the present procedure, an exponentially decaying curve of the absorbance of the boron–hydrogen bridges was observed. This also suggested that the reaction followed first-order kinetics. Six representative points on this exponentially decaying curve were selected and the corresponding first-order rate constants calculated (Table I). Clearly, the first-order rate constants remained virtually unchanged throughout the reaction. In addition, the first-order rate constants remained essentially the same as the initial concentrations of $(9\text{-BBN})_2$ and cyclopentene were varied (Table II).

The same exponentially decaying curve was also observed with several other more reactive alkenes such as 2-methyl-1-pentene, 1-hexene, and 3,3-dimethyl-1-butene. The corresponding first-order rate constants were calculated and listed in Table III. Very good agreement is realized between these first-order rate constants for various alkenes. More importantly, they are also in very good agreement with the corresponding first-order rate constants obtained by the quenching method (Table III).

The reaction of $(9\text{-BBN})_2$ with these more reactive alkenes in other solvents such as THF, cyclohexane, benzene, and diethyl ether was also studied. Similar exponentially decaying curves and the first-order kinetics were observed. A list of the first-order rate constants is given in Table III. Again, good agreement with the corresponding first-order rate constants obtained by the quenching method is realized (Table III).

Table III. First-Order Rate Constants for the Hydroboration of Representative Alkenes with $(9\text{-BBN})_2$ in Various Solvents at 25 °C

	10^4k_1, s^{-1} [a]				
alkene	CCl_4	THF	cyclohexane	benzene	Et_2O
1-hexene	1.54 (1.53)	13.9 (14.2)	1.51 (1.45)	2.05	2.83
2-methyl-1-pentene	1.46 (1.54)	13.7 (14.3)	1.51 (1.51)	1.99	2.81
3,3-dimethyl-1-butene	1.45 (1.45)	14.0 (13.2)	1.48 (1.43)	2.02	2.80
cyclopentene	1.54 (1.52)	11.8 (10.8)[b]	1.46 (1.52)	2.06	2.77

[a] Numbers in the parentheses were obtained by the quenching method. [b] The reaction is not a clean first-order reaction and starts to show intermediate kinetic behavior in THF solvent.

Table IV. Rate Data and Rate Constants for the Hydroboration of Cyclohexene (0.400 M) with $(9\text{-BBN})_2$ (0.200 M) in Carbon Tetrachloride at 25 °C

t, s	$[(9\text{-BBN})_2]_t$,[a] M	[cyclohexene], M	$10^4 k_{3/2}$,[b,c] $M^{-1/2}\ s^{-1}$
0	0.200	0.400	
12 000	0.148	0.295	0.307
18 000	0.129	0.258	0.304
24 000	0.114	0.228	0.303
30 000	0.101	0.202	0.303
42 000	0.081	0.161	0.308
72 000	0.049	0.098	0.316

[a] Calculated from eq 7. [b] Calculated from the equation $k_{3/2}t = 2^{1/2}[(b - 2x)^{-1/2} - b^{-1/2}]$, where b is the initial concentration of cyclohexene and $b = 2x$ is the concentration at time t. [c] The $^3/_2$-order rate constant obtained by the quenching method is $0.323 \times 10^{-4}\ M^{-1/2}\ s^{-1}$.

Three-Halves-Order Kinetics. Previous studies revealed that the rate of the hydroboration of cyclohexene with $(9\text{-BBN})_2$ in CCl_4 is much slower than that of cyclopentene. The reaction also exhibited $^3/_2$-order kinetics, first-order in cyclohexene and half order in $(9\text{-BBN})_2$ (eq 6).

$$-d[(9\text{-BBN})_2]/dt = k_{3/2}[(9\text{-BBN})_2]^{1/2}[\text{cyclohexene}] \qquad (6)$$

These characteristics were also observed by the present procedure. The rate of the disappearance of the absorbance of boron–hydrogen bridges of $(9\text{-BBN})_2$ was much slower. In addition, this decaying curve was found to fit $^3/_2$-order kinetics. Six representative points were selected from this decaying curve and the corresponding $^3/_2$-order rate constants calculated (Table IV). Clearly, the $^3/_2$-order rate constants remained virtually unchanged. Moreover, these $^3/_2$-order rate constants are in very good agreement with those obtained by the quenching method (Table IV). Varying the initial concentrations of $(9\text{-BBN})_2$ and cyclohexene afforded essentially the same $^3/_2$-order rate constants (Table II).

Intermediate Kinetics. It was previously observed that 2-methyl-2-butene and *cis*-3-hexene exhibit intermediate kinetic behavior between that of first-order and $^3/_2$-order kinetics. This is also the case observed by the infrared method. A list of the typical data for *cis*-3-hexene is given in Table II. They fit neither first-order nor $^3/_2$-order integrated kinetic expressions.

Reaction Mechanism. The very good agreement between the reaction kinetics observed by the quenching method and the infrared method further supported the proposed dissociation mechanism for the reaction of alkenes with $(9\text{-BBN})_2$ (eq 1 and 2). A detailed discussion using this mechanism to account for the observed kinetics was given previously.[1] Apparently, for the more reactive alkenes such as cyclopentene, 2-methyl-1-pentene, 1-hexene, and 3,3-dimethyl-1-butene, the rate-determining step is the dissociation of the dimer (eq 1). Therefore, the reaction exhibits first-order kinetics (eq 5). For the less reactive alkenes such as cyclohexene, the reaction of alkenes with the monomer becomes the rate-determining step (eq 2). Therefore, the reaction exhibits $^3/_2$-order kinetics (eq 6). For certain alkenes, such as 2-methyl-2-butene and *cis*-3-hexene, neither of these two steps is a decisive rate-determining step. Therefore, the reaction exhibits intermediate kinetic behavior between that of first-order and $^3/_2$-order kinetics.

Conclusion

A convenient method for following the hydroboration reaction by using a quantitative infrared spectrometer has been developed. Its application to the study of hydroboration of alkenes with $(9\text{-BBN})_2$ further confirmed the earlier proposed dissociation mechanism. This technique can also be readily applied to many other reactions of $(9\text{-BBN})_2$. The reaction rates of $(9\text{-BBN})_2$ with other substrates such as alkynes, aldehydes, ketones, and amines can be easily studied. In addition, the reactions with other organoborane reagents can be similarly followed. Therefore, we are now in a position to rapidly explore the kinetics of the reactions of organoboranes. Hopefully, this will lead to a complete understanding of the reaction mechanisms.

Experimental Section

General Methods. General procedures for the manipulation of boron reagents have been outlined in chapter 9 of ref 4c. All glassware, syringes, and needles were oven dried at 140 °C for several hours. The glassware was assembled while hot and cooled under a stream of dry nitrogen. Syringes were assembled and fitted with needles while hot and then cooled as assembled units.

Materials. The preparation of $(9\text{-BBN})_2$ was carried out as described previously.[8] Further recrystallization from monoglyme affords very pure product.[11] The solvents were purified before use. The alkenes were distilled under nitrogen from lithium aluminum hydride and then stored under nitrogen.

Instruments. A Miran-1A variable-filter infrared spectrometer from Wilks Scientific Corp. was used to monitor the boron–hydrogen bridges of $(9\text{-BBN})_2$ at 1570 cm^{-1}. The reaction mixture was pumped at 4 mL/min through a 0.10-mm Wilks NaCl precision sealed cell mounted on a stainless-steel holder. The inlet and the outlet of the cell were equipped with a Hamilton valve No. 2X male Luer connector. The inlet was connected with a 20-in. stainless-steel hypodermic needle (gauge 20). The needle penetrated into the reaction flask through a rubber septum on a side-arm inlet. The outlet of the cell was connected to the inlet of a Rhickc miniature pump head from Fluid Metering Inc. by using a double-ended needle with a standard metal hub on both ends. The outlet of the pump head was connected back to the reaction flask through a 20-in. stainless-steel hypodermic needle (gauge 20). The pump head was driven by an electric motor. The absorbance of the reaction mixture was recorded on a Hewlett-Packard 71274 strip chart recorder. The validity of Beer's law was tested for the concentrations between 0.0125 M and 0.200 M of $(9\text{-BBN})_2$. A linear relationship between absorbance and concentration was observed.

Kinetics Procedure. A typical example of the quantitative infrared procedure is as follows. A 100-mL flask with a side-arm inlet and a magnetic stirring bar was dried in an oven (140 °C, 4 h) and cooled to room temperature under a stream of dry nitrogen. The flask was immersed in a temperature-controlled water bath (25.00 ± 0.05 °C). Then 6.7 mL of dry CCl_4 was injected into the reaction flask followed by 17.4 mL of $(9\text{-BBN})_2$ solution (0.288 M, 5.00 mmol) in CCl_4. The mixture was stirred for 20 min to equilibrate to the bath temperature and was then pumped through the infrared cell to determine the absorbance. The reaction was initiated by adding 0.681 g of cyclopentene (0.88 mL, 10.0 mmol) into the reaction mixture. The initial concentrations of $(9\text{-BBN})_2$ and cyclopentene were 0.200 and 0.400 M, respectively.

The reaction was followed by monitoring the rate of the disappearance of boron–hydrogen bridges of $(9\text{-BBN})_2$ at 1570 cm^{-1}. The absorbance stopped decreasing after 10 h as $(9\text{-BBN})_2$ was all reacted. The reaction flask was removed, and CCl_4 solvent was pumped through the cell to determine the background absorbance. The background absorbance of pure solvent was essentially the same as the residual absorbance of the reaction mixture. The data from this study was summarized in Table I.

Calculations. The concentration of $(9\text{-BBN})_2$ at a given reaction time was calculated accordng to eq 7, where $[(9\text{-BBN})_2]_0$

$$[(9\text{-BBN})_2]_t = [(9\text{-BBN})_2]_0((c - b)/(a - b)) \qquad (7)$$

is the initial concentration of $(9\text{-BBN})_2$, $[(9\text{-BBN})_2]_t$ is the con-

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(11) Brown, H. C.; Soderquist, J. A., unpublished results.

centration of $(9\text{-BBN})_2$ at time t, a is the initial absorbance, c is the absorbance at time t, and b is the background absorbance.

The calculations of the rate constants were carried out on a Hewlett-Packard 9820 calculator. The concentrations were substituted into the integrated rate expressions appropriate for each kinetic order. The best straight line was fitted to each set of points by using the method of least squares. The rate constants for the different kinetic orders were obtained numerically as the slopes of the lines.

Registry No. 9-Borabicyclo[3.3.1]nonane dimer, 70658-61-6; cyclopentene, 142-29-0; cyclohexene, 110-83-8; *cis*-3-hexene, 7642-09-3; 1-hexene, 592-41-6; 2-methyl-1-pentene, 763-29-1; 3,3-dimethyl-1-butene, 558-37-2.

Relative Rates and Regioselectivity in the Hydroboration of Substituted Styrenes with 9-Borabicyclo[3.3.1]nonane in Tetrahydrofuran

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The relative rates of reaction of *p*-CH_3O, *p*-CH_3, unsubstituted, *p*-F, *p*-Cl, *m*-Cl, and *m*-NO_2 styrenes with 9-borabicyclo[3.3.1]nonane (9-BBN) in THF solution at 25 °C have been determined to be 2.95, 1.51, 1.00, 0.89, 0.69, 0.63, and 0.60. The relative rates were established by allowing a mixture of styrene and the substituted styrene to react with a limited amount of 9-BBN (GLC analysis). A Hammett plot, using σ^+, is reasonably linear with $\rho = -0.49$, corresponding to a small buildup of positive charge at the α-carbon of the styrene and reaction with the $B^{\delta+}$–$H^{\delta-}$ bond. 9-BBN gives high regioselectivity in its reactions with the six styrenes tested, the β-phenylethyl alcohol being formed to the extent of 97.4% or higher in all cases. The large steric requirements of the 9-BBN result in the orientation of the B–H bond with B away from the aromatic ring. Several 9-BBN adducts of substituted styrenes have been prepared in pure form.

9-Borabicyclo[3.3.1]nonane (9-BBN)[1,2] has been shown by Brown and co-workers[2-4] to be an exceptionally versatile hydroborating reagent, easy to handle as the dimeric solid (even in air) and in solution (nitrogen atmosphere required), and of great thermal stability. For reactive alkenes, hydroboration rates have recently been shown[5] to be first order in 9-BBN dimer and independent of alkene concentration (rate-determining dissociation of the dimer), while for less reactive olefins, the rates are half order in 9-BBN dimer and first order in alkene (rate-determining reaction of the 9-BBN monomer with the alkene). Thus, in order to assess the relative reactivities of alkenes, it is necessary to use competitive experiments where mixtures of alkenes react with a limited amount of 9-BBN.[6] From these previous experiments[6] it is clear that the rates of reaction of 9-BBN are subject to large steric effects but that 9-BBN is nevertheless quite sensitive to electronic influences, presumably due to the strained bridging >BH moiety. For instance, using the competitive technique, Brown, Liotta, and Scouten[6] showed that *p*-methoxystyrene, unsubstituted styrene, and *p*-(trifluoromethyl)styrene had relative reactivities of 14.0:1:0.2 toward 9-BBN, whereas Klein, Dunkelblum, and Wolff[7] found that the overall rate of reaction of styrenes with diborane changes very little with substituents ranging from methoxy to chloro. As a first step in a projected isotope effect study of the mechanisms of hydroboration of substituted styrenes, we have extended the competitive rate experiments of 9-BBN to include reactions with several additional substituted styrenes.

Scheme I

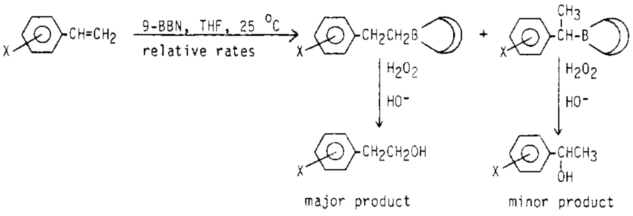

Table I. Relative Reactivities of Substituted Styrenes toward 9-BBN in THF at 25 ± 0.1 °C

substituent	k_X/k_H ± std dev	substituent	k_X/k_H ± std dev
p-CH_3O	2.95 ± 0.22	*p*-Cl	0.69 ± 0.01
p-CH_3	1.51 ± 0.04	*m*-Cl	0.63 ± 0.02
none	1.00	*m*-NO_2	0.60 ± 0.04
p-F	0.89 ± 0.03		

One of the most useful features of 9-BBN is its extremely high regioselectivity in hydroboration reactions.[3,8,9] For instance, in the diborane hydroboration–alkaline hydrogen peroxide oxidation of styrene, 2-phenylethanol and 1-phenylethanol were formed[10,11] in 81% and 19% relative yields, while with 9-BBN the relative yields were 98.5% and 1.5%.[3,8,9] For optimum usefulness and ease of interpretation, our projected isotope effect study required a reaction proceeding to only one product, and it was hoped that 9-BBN reactions with substituted styrenes would also be highly regioselective. Since the regioselectivity of the reactions of 9-BBN with substituted styrenes did not seem to have been reported, we have carried out such a study.

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