Organoboron Compounds. XIX. Kinetics of the Thermal Isomerization of α-Branched Trialkylboranes[1,2]

FRANCES M. ROSSI, PATRICK A. MCCUSKER, AND G. F. HENNION

Department of Chemistry and Radiation Laboratory,[3] University of Notre Dame, Notre Dame, Indiana 46556

Received September 27, 1966

Kinetic data for the thermal isomerization of *t*-butyldiisobutylborane to triisobutylborane and for the stepwise isomerization of triisopropylborane and of tri-*sec*-butylborane to the corresponding tri-*n*-alkylboranes have been obtained over a range of temperatures. First-order kinetics were observed in all cases. The specific reaction rates were found to be the same whether the reactions were carried out neat, in end-product trialkylborane, or in diglyme as solvent. Enthalpies and entropies of activation derived from the rate data are consistent with the assumption that the mechanism of the reaction involves virtually complete disengagement of an alkyl group as olefin in the case of *t*-butyldiisobutylborane but only partial disengagement in the case of the secondary trialkylboranes. The specific reaction rates for the stepwise isomerization of triisopropylborane are in the ratio of 3:2:1, indicating that the rate of isomerization of a single isopropyl group is unaffected by the nature of the other groups attached to boron. The enthalpies of activation for the three steps in the isomerization of triisopropylborane are the same, the differences in rates being due to differences in the entropies of activation.

Although the thermal isomerization of α-branched alkyl groups to primary alkyl groups in trialkylboranes has been known since 1955[4,5] and mechanisms have been suggested for the reaction,[5-8] no kinetic data have been reported for the process. The present work was undertaken to obtain such data as an aid for the evaluation of the proposed mechanisms. Specific rate constants for the isomerization of *t*-butyldiisobutylborane to triisobutylborane, for the stepwise isomerization of triisopropylborane to tri-*n*-propylborane and for the isomerization of secondary to normal butyl groups in tri-*sec*-butylborane have been obtained at a series of temperatures in the range 120–150°. It should be noted that this range is essentially the same as that for the exchange reaction of trialkylboranes with olefins, the well-known "displacement reaction."[9] A mechanism is now proposed which is consistent with the kinetic parameters and with what is known about the displacement reactions.

Results and Discussion

The specific reaction rate constants obtained for the various trialkylboranes are listed in Table I.

The data obtained for the isomerization of *t*-butyldiisobutylborane to triisobutylborane at 138° are given graphically in Figure 1 and show that the process is clearly first and not second order. Similar plots of data for the other trialkylboranes gave the same result.

The stepwise isomerization of triisopropylborane, *via* diisopropyl-*n*-propylborane and isopropyldi-*n*-propylborane, to tri-*n*-propylborane is presented graphically in Figure 2. This graph shows the pattern characteristic of a series of consecutive first-order processes.

TABLE I

SPECIFIC RATE CONSTANTS FOR THE THERMAL ISOMERIZATION OF TRIALKYLBORANES

Entry	Reaction	*T*, °C	Solvent	$k \times 10^3$, hr^{-1}
1	$(t\text{-Bu})B(i\text{-Bu})_2 \longrightarrow (i\text{-Bu})_3B$	120	None	9.0 ± 0.4
2		120	$(i\text{-Bu})_3B$	9.0 ± 0.4
3		130	$(i\text{-Bu})_3B$	26.1 ± 0.6
4		138	None	65 ± 9
5		138	$(i\text{-Bu})_3B$	65 ± 3
6		138	Diglyme	65 ± 5
7		145	None	168 ± 3
8		150	None	277 ± 18
9		150	$(i\text{-Bu})_3B$	264 ± 18
10	$(i\text{-Pr})_3B \longrightarrow (i\text{-Pr})_2B(n\text{-Pr})$	121	None	35 ± 2
11		128	None	63 ± 4
12		135	None	123 ± 11
13	$(i\text{-Pr})_2B(n\text{-Pr}) \longrightarrow (i\text{-Pr})B(n\text{-Pr})_2$	128	None	36 ± 6
14		135	None	69 ± 1
15	$(i\text{-Pr})B(n\text{-Pr})_2 \longrightarrow (n\text{-Pr})_3B$	128	None	21 ± 1
16		135	None	39 ± 1
17	$i\text{-Pr} \longrightarrow n\text{-Pr}$ (over-all)	135	None	39 ± 1
18	$(sec\text{-Bu})B(n\text{-Bu})_2 \longrightarrow (n\text{-Bu})_3B$	125	None	21 ± 1
19		130	None	35 ± 2
20		135	None	60 ± 2
21		145	None	154 ± 7
22		150	None	240 ± 13

The rate constants for the three steps in the over-all reaction were calculated from the analytically observed concentrations of the four compounds by the classical method for consecutive first-order processes.[10] The method of calculation gives fairly precise values for the rate constant, k_a, for the first step in the process, but accumulation of errors makes the values of the second- and third-step constants (k_b and k_c) less reliable. To obtain more reliable values for the rate constant for the third step, a sample consisting largely of isopropyldi-*n*-propylborane was isomerized at 128 and at 135° and the rate constants, k_c, were calculated, making allowance for the reversibility of the process reported previously from this laboratory.[11] From the quite reliably determined

---

[1] Previous paper: P. A. McCusker and J. H. Bright, *J. Inorg. Nucl. Chem.*, **28**, 2261 (1966).

[2] Abstracted from the doctoral dissertation of F. M. Rossi.

[3] The Radiation Laboratory of the University of Notre Dame is operated under contract with the U. S. Atomic Energy Commission. This is AEC document COO-38-486.

[4] G. F. Hennion, P. A. McCusker, E. C. Ashby, and A. J. Rutkowski, Abstracts, 130th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1956, p 53-O.

[5] G. F. Hennion, P. A. McCusker, E. C. Ashby, and A. J. Rutkowski, *J. Am. Chem. Soc.*, **79**, 5190 (1957).

[6] H. C. Brown and B. C. Subba Rao, *J. Org. Chem.*, **22**, 1137 (1957).

[7] G. F. Hennion, Dissertation of J. V. Marra, University of Notre Dame, 1959, p 136.

[8] H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **88**, 1433 (1966).

[9] H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1962, p 153.

[10] E. A. Moelwyn-Hughes, "Physical Chemistry," Pergamon Press Ltd., London, 1957, p 226.

[11] P. A. McCusker, F. M. Rossi, J. H. Bright, and G. F. Hennion, *J. Org. Chem.*, **28**, 2889 (1963).

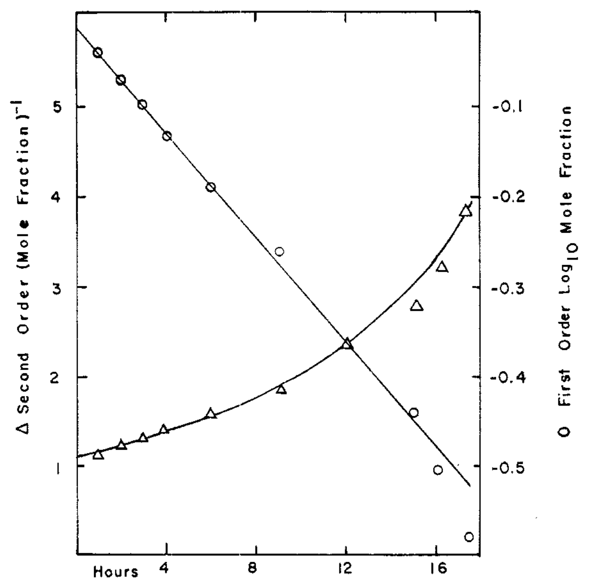


Figure 1.—Kinetic order of isomerization reaction of *t*-butyldiisobutylborane at 138°.

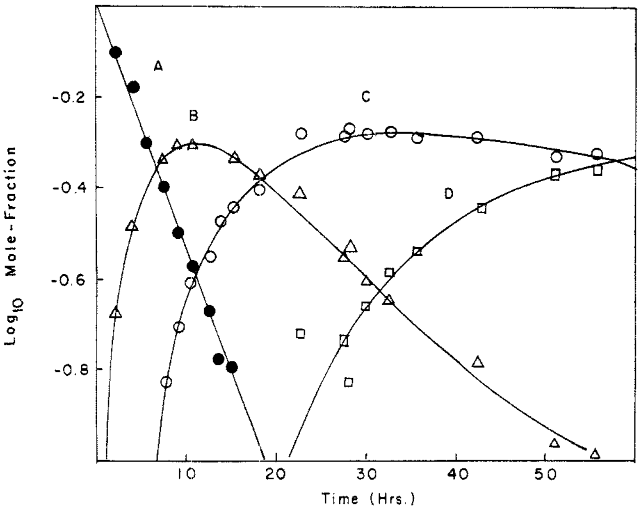


Figure 2.—The thermal isomerization of triisopropylborane at 135°: A, $(i\text{-Pr})_3B$; B, $(i\text{-Pr})_2(n\text{-Pr})B$; C, $(i\text{-Pr})(n\text{-Pr})_2B$; D, $(n\text{-Pr})_3B$.

values of k_a and k_c it was found that the ratio k_a/k_c is 3.0 within experimental error. The value obtained for k_b was observed to be two-thirds that of k_a, again within experimental error. Thus the k_a:k_b:k_c ratio is found to be 3:2:1.

The isomerization of isopropyl groups in propylboranes to *n*-propyl groups was also followed in separate runs by analysis for alkyl groups through alkaline oxidation and alcohol ratio determination. From these data the over-all rate of isomerization of isopropyl to *n*-propyl groups was calculated (Table I, entry 17). The rate data for over-all isomerization at 135° are shown graphically in Figure 3. The rate constant determined from these data was found to be identical, as listed in Table I, with the independently determined rate constant for the isomerization of isopropyldi-*n*-propylborane to tri-*n*-propylborane. The 3:2:1 rate ratio shows that relief of steric strain is not a kinetic driving force for alkyl group isomerization.

Because of analytical difficulties encountered in the gas chromatographic separation of the four isomeric secondary–normal tributylboranes, determination of alkyl group ratios only were made in this system. On the basis of the results obtained in the propyl case, the rate constant for the secondary to normal butyl group isomerization was taken as equal to that for the third step in the stepwise isomerization, *i.e.*, the isomerization of *sec*-butyldi-*n*-butylborane to tri-*n*-butylborane. The values for the rate constants for the first two steps were calculated on the assumption that the same ratio of rate constants holds for the secondary butyl case as was found for the isopropyl case.

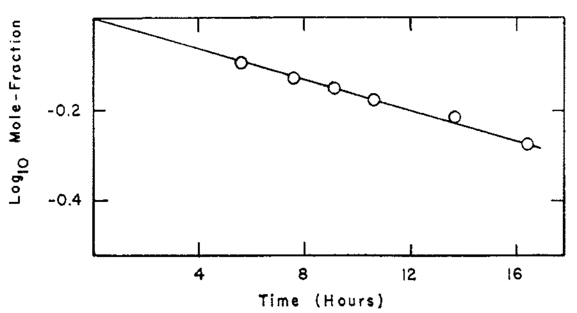


Figure 3.—Rate of decrease of total isopropyl groups in the isomerization of triisopropylborane; $k_1 = 0.04\ \text{hr}^{-1}$ at 135°.

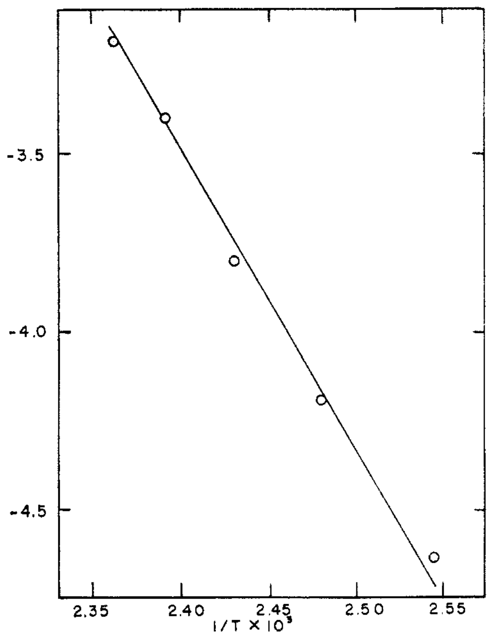


Figure 4.—Temperature dependence of the rate constant for thermal isomerization of *t*-butyldiisobutylborane.

From the specific rate constants at the several temperatures the kinetic parameters, ΔH^* and ΔS^*, were calculated from the Eyring equation, $k_r = k'T/h \cdot e^{\Delta S^*/R} \cdot e^{-\Delta H^*/RT}$, using the method of least squares. The errors in ΔS^* were estimated on the basis of the errors in ΔH^*. The kinetic parameters are listed in Table II. The set of data used for the calculation of kinetic parameters for the case of *t*-butyldiisobutylborane is shown graphically in Figure 4 for purposes of illustration.

The kinetic parameters for the isomerization of *t*-butyldiisobutylborane to the triisobutyl compound and those for the comparable isomerization of isopropyldi-*n*-propylborane and *sec*-butyl-di-*n*-butylborane to the tri-*n*-alkyl isomers differ sufficiently to warrant the assumption of at least a qualitative difference in the

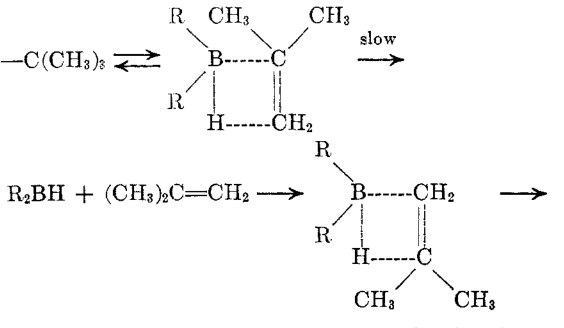
TABLE II

KINETIC PARAMETERS FOR THE THERMAL ISOMERIZATION OF TRIALKYLBORANES

Entry	Reaction	ΔH^*, kcal/mole	ΔS^*, eu
1	$(t\text{-Bu})B(i\text{-Bu})_2 \longrightarrow (i\text{-Bu})_3B$	39 ± 1.1	14.2 ± 2.6
2	$(i\text{-Pr})_3B \longrightarrow (i\text{Pr})_2B(n\text{-Pr})$	29 ± 1.5	-8.5 ± 3.5
3	$(i\text{-Pr})_2B(n\text{-Pr}) \longrightarrow (i\text{-Pr})B(n\text{-Pr})_2$	29 ± 1.5	-9.3 ± 3.5
4	$(i\text{-Pr})B(n\text{-Pr})_2 \longrightarrow (n\text{-Pr})_3B$	29 ± 1.5	-10.7 ± 3.5
5	$(sec\text{-Bu})_3B \longrightarrow (sec\text{-Bu})_2B(n\text{-Bu})$	$(31.7 + 0.2)^a$	-1.2 ± 0.4
6	$(sec\text{-Bu})_2B(n\text{-Bu}) \longrightarrow (sec\text{-Bu})B(n\text{-Bu})_2$	$(31.7 \pm 0.2)^a$	-2.0 ± 0.5
7	$(sec\text{-Bu})B(n\text{-Bu})_2 \longrightarrow (n\text{-Bu})_3B$	31.7 ± 0.2	-3.5 ± 0.5

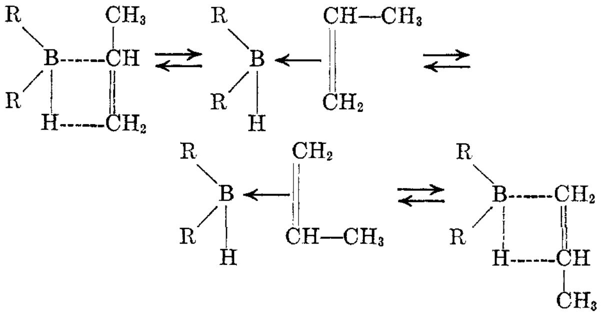
[a] Assumed to be equal to the value in entry 7; see the discussion.

mechanisms of these reactions. The ΔH^* for *t*-butyl → isobutyl is 39 kcal/mole while isopropyl → *n*-propyl and *sec*-butyl → *n*-butyl have values of 29 and 32 kcal/mole, respectively. The ΔS^* values differ even more significantly: for *t*-butyl → isobutyl, +14 eu; for isopropyl → *n*-propyl, −10 eu; and for *sec*-butyl → *n*-butyl, −3 eu. Thus ΔS^* spans values ranging from large and positive to large and negative. On the one extreme, the irreversible[11] isomerization of *t*-butyldiisobutylborane to triisobutylborane (Table II, entry 1), the mechanism would appear to be as shown in eq 1.



$R_2BCH_2CH(CH_3)_2$ (1)

At the other extreme, as in the reversible[11] isomerization of isopropyldi-*n*-propylborane to tri-*n*-propylborane (Table II, entry 4), the mechanism *must* differ in that the olefin apparently remains bound in some manner throughout. An obvious variation of the mechanism shown (eq 1) is one in which the four-membered ring collapses to a π complex in which rotational inversion leads to the isomeric ring intermediate (eq 2). There may well be intermediate degrees of olefin restraint or freedom during isomerization; thus one can imagine a spectrum of unimolecular reactions having the variations of activation parameters as were observed.[12] There are obvious real differences in isopropyl and *t*-butyl relative to the degree of olefin disengagement. In the case of isobutylene from *t*-butyl, the incipient double bond is stabilized by two methyl groups; furthermore the rupture of the four-membered ring may be assisted by steric crowding. Propylene from isopropyl has the incipient double bond stabilized by only one methyl and collapse to a π complex, rather than rupture, may be sterically and electronically more favorable. It may be pointed out also that, while ΔH^* and ΔS^* vary markedly for the various reactions, the ΔG^* values are nearly the same, in the final isomerization step, for all cases over the temperature range investigated.



(2)

Experimental Section

t-Butyldiisobutylborane, triisobutylborane, triisopropylborane, and tri-*sec*-butylborane were prepared according to previously described procedures.[5,13] A mixture containing 70% isopropyldi-*n*-propylborane and 30% tri-*n*-propylborane was obtained by distillation at low temperature of a partially isomerized mixture of tripropylboranes. The products were, in most cases, treated with strong base to ensure removal of oxidation products and were distilled through spinning-band columns to give fractions with boiling ranges of less than 0.3°. In all operations an atmosphere of dry nitrogen was maintained over the trialkylboranes.

The apparatus used in the kinetic studies consisted of a 25-ml, three-necked flask equipped with a water-cooled condenser, connected by a T tube to a source of nitrogen and to sulfuric acid bubblers. The trialkylboranes, with or without solvent, were introduced into the reaction vessel by means of dry nitrogen. A side neck was fitted with a capillary tube extending from the bottom of the reaction flask through a condenser to a 10-ml, removable sampling flask, which was swept out with nitrogen after each sampling. At time intervals, 6–9 drops of sample was collected, quenched with a Dry Ice–acetone bath, and analyzed. Temperatures were maintained constant to 0.1°.

The composition of the isomeric mixtures containing triisopropylborane, diisopropyl-*n*-propylborane, isopropyldi-*n*-propylborane, and tri-*n*-propylborane were determined directly by glpc. The four components were resolved on a 2-m column of silicone 550 at 95° with a flow rate of 110 ml of He/min. Triisopropylborane and tri-*n*-propylborane were identified by comparison with synthetic mixtures. The other two components were taken to be the redistribution products by comparison of their retention times with those reported by Koster[14] who identified the four components by mass spectrometry. Confirmation of the identity of the two unsymmetrical trialkylboranes was obtained by comparing the calculated ratio of isopropyl to normal propyl groups with that observed following oxidation of the samples and quantitative glpc analysis for the resulting alcohols.

The mixtures of butylboranes were oxidized by alkaline hydrogen peroxide; the resulting isomeric alcohols were analyzed by glpc on a 1.5-m Carbowax 20 M column at a temperature programmed from 75 to 100° and at a flow rate of 75 ml of He/min. Synthetic mixtures of the various butyl alcohols were used for standardization.

---

(12) Trialkylborane isomerizations catalyzed[8] by diborane or by hydroborane species likely involve reactions other than (and/or in addition to) those here discussed (*e.g.*, $R_3B + BH_3 \rightarrow R_2BH + RBH_2$; $RBH_2 + R_3B \rightarrow 2R_2BH$; $R_2BH \rightarrow RBH_2 +$ olefin; etc.) and some of these reactions may involve bridged dimers. Though trace amounts of BH species may have been unavoidably present in our samples, the amounts certainly were insufficient to induce isomerization since the compounds used were completely stable to isomerization over periods of several months at room temperature.

(13) G. F. Hennion, P. A. McCusker, and A. J. Rutkowski, *J. Am. Chem. Soc.*, **80**, 617 (1958).

(14) G. Schomberg, R. Koster, and D. Henneberg, *Z. Anal. Chem.*, **170**, 285 (1959).