give $B_2H_5NH_2$. These facts show that BH_2NH_2 is not formed through NH_3 in the present reaction.

The comparison of B–O and B–N lengths obtained for $B_3H_4NO_2$ and $B_3H_5N_2O$ with those for similar compounds shows that the change in B–O and B–N bond lengths has different trends. Both the B–O lengths found in the two molecules are around 1.385 Å, and this value is almost the same as that of boroxin.[10] On the other hand, the two B–N lengths in $B_3H_5N_2O$ are fairly different: 1.412 and 1.432 Å. The smaller one is the same as the B–N length in $B_3H_4NO_2$, 1.412 Å, and the larger one is close to that in borazine, 1.4355 (40) Å.[11] The shortening of the B–O bond adjacent to the O atom may be ascribed to the conjugation between B–N and B–O bonds. It is interesting to compare the B–N lengths with those in BH_2NH_2, 1.391 Å,[13] and in $BH(NH_2)_2$, 1.418 (1) Å.[17] Since borane is an electron-deficient molecule and amine has a lone pair, the B–N bonds in above molecules have large double-bond character, and the amount of double-bond character seems to decrease in the order BH_2NH_2, $BH(NH_2)_2$, $B_3H_4NO_2$, $B_3H_5N_2O$, and borazine.

Registry No. B_2H_6, 19287-45-7; NO, 10102-43-9; BH_2NH_2, 14720-35-5; $B_2H_5NH_2$, 39046-41-8; N_2O, 10024-97-2; B_2D_6, 20396-66-1; ^{15}NO, 15917-77-8; $B_3H_5N_2O$, 118496-08-5; $B_3H_4NO_2$, 118496-03-0; $B_3H_4NO_2$-*3*-^{15}N, 118496-04-1; $B_3H_4NO_2$-*2*-^{10}B, 118496-05-2; $B_3H_4NO_2$-*6*-^{10}B, 118496-06-3; $B_3D_4NO_2$, 118496-07-4; $B_3H_5N_2O$-*1,5*-$^{15}N_2$, 118496-09-6; $B_3H_5N_2O$-*6*-^{10}B, 118496-10-9; $B_3H_5N_2O$-*2*-^{10}B, 118496-11-0.

Supplementary Material Available: Tables of observed transition frequencies for nine isotopic species (9 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
California State University, Los Angeles, California 90032

Thermal Rearrangement Studies on Ethyl and Chloro Diethyl Derivatives of *closo*-2,4-$C_2B_5H_7$: Elimination of a 1,2-Substituent-Shift Mechanistic Hypothesis and Further Support of the DSD Cage Rearrangement Mechanism

Wonwoo Nam, Zahid J. Abdou, Han Lee, Tereso Banuelos, and Thomas Onak*

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The thermal (295–340 °C) rearrangement pattern for 3-Cl-5,6-$(C_2H_5)_2$-*closo*-2,4-$C_2B_5H_4$ supports a DSD cage mechanism but, more importantly, rules out a 1,2-substituent-shift mechanism. The rate constants for the 295 °C rearrangement of 5-C_2H_5-*closo*-2,4-$C_2B_5H_6$ and 5,6-$(C_2H_5)_2$-*closo*-2,4-$C_2B_5H_5$ are determined, and equilibrium percentages of the three *B*-C_2H_5-2,4-$C_2B_5H_6$ isomers and the five *B,B'*-$(C_2H_5)_2$-2,4-$C_2B_5H_5$ isomers are obtained.

Introduction

Kinetic studies on the rearrangements of mono- and dimethyl derivatives,[1-3] mono- and dichloro derivatives,[3-5] mono- and dibromo derivatives,[6] and mono- and diiodo derivatives[6] of 2,4-$C_2B_5H_7$ have been reported. Among three plausible rearrangement mechanisms (Figure 1 illustrates the various mechanistic models) for the above substituted *closo*-2,4-$C_2B_5H_7$ compounds—diamond–square–diamond (DSD),[7-9] triangle face rotation (TFR),[8,10] and surface-substituent migration (SSM, also known as 1,2-substituent-shift mechanism)[10]—it appears that the TFR mechanism can be ruled out.[2,3,5,6] It should be mentioned that previous considerations of the DSD and TFR mechanisms (above references) have argued the common constraint: cage carbon atoms are returned to low-coordination nonadjacent positions of the *closo*-dicarbaheptaborane polyhedron after each cage-movement cycle.

In the present study, a rearrangement of 3-Cl-5,6-$(C_2H_5)_2$-2,4-$C_2B_5H_4$ has been conducted in an attempt to differentiate between the DSD and 1,2-substituent-shift mechanisms. In addition, kinetic studies have been carried out on mono- and diethyl derivatives of the same cage carborane. Relative stabilities within each isomer set are evaluated and correlated.

Experimental Section

Materials and Handling of Chemicals. The parent carborane *closo*-2,4-$C_2B_5H_7$, obtained from R. E. Williams, was used without further purification, and 3-Cl-2,4-$C_2B_5H_6$ was prepared according to a literature procedure.[11] Aluminum trichloride (Aldrich Chemical Company Inc.) was sublimed directly into the reaction vessel prior to use. Chloroethane (Matheson) was used without further purification. All materials were handled by using conventional high-vacuum techniques or in a nitrogen drybox. Purification of volatile compounds was accomplished either by cold-column separation[12] or by trap-to-trap fractionation in a standard high-vacuum apparatus.[13]

Nuclear Magnetic Resonance. Boron-11 (160.44 MHz) NMR data, Table I, were gathered by using a Bruker WM-500 FT spectrometer at the California Institute of Technology, Pasadena, CA, and a Bruker AM-400 FT spectrometer at CSULA. All ^{11}B chemical shift data are based on $\delta(BF_3{\cdot}Et_2O) = 0.00$ ppm, with 2,4-$C_2B_5H_7$ used as a secondary standard, with $\delta(1,7) = -21.73$ ppm, $\delta(3) = +7.02$ ppm, and $\delta(5,6) = +3.83$ ppm. Negative chemical shift values are upfield of the $BF_3{\cdot}OEt_2$ resonance. Approximate chemical shift and coupling constant errors for all dicarbaheptaboranes are as follows: ±0.02 ppm and ±3 Hz, for the 1, 3, and 7 cage positions of the carborane; ±0.06 ppm, ±10 Hz, for the 5 and 6 cage positions. Proton (60 MHz) NMR spectra were obtained

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Table I. ^{11}B NMR Data for B-C_2H_5-2,4,-$C_2B_5H_6$, B,B'-$(C_2H_5)_2$-2,4-$C_2B_5H_5$, and B-Cl-B',B''-$(C_2H_5)_2$-2,4-$C_2B_5H_4$ Derivatives[a]

compd	chem shift, ppm				
	B(1)	B(3)	B(5)	B(6)	B(7)
1-C_2H_5-2,4-$C_2B_5H_6$	−9.74	7.67 (180)	3.73 (166)	3.73 (166)	−27.63 (181)
3-C_2H_5-2,4-$C_2B_5H_6$	−20.68 (179)	15.57	3.28 (172)	3.28 (172)	−20.68 (179)
5-C_2H_5-2,4-$C_2B_5H_6$	−21.29 (178)	6.40 (184)	13.45	1.93 (169)	−21.29 (178)
1,3-$(C_2H_5)_2$-2,4-$C_2B_5H_5$	−9.41	15.84	3.36 (168)	3.36 (168)	−26.30 (175)
	[−8.69]	[16.22]	[3.18]	[3.18]	[−26.58]
1,5-$(C_2H_5)_2$-2,4-C_2H_5Hb	−9.46	7.09 (18)	13.15	1.69 (165)	−26.95 (177)
	[−9.30]	[7.05]	[13.35]	[1.83]	[−27.19]
1,7-$(C_2H_5)_2$-2,4-$C_2B_5H_5$	−15.68	8.64 (186)	3.7	3.7	−15.68
	[−15.64]	[8.32]	[3.63]	[3.63]	[−15.64]
3,5-$(C_2H_5)_2$-2,4-$C_2B_5H_5$	−20.16 (175)	15.0	13.2	1.23 (165)	−20.16 (175)
	[20.24]	[14.95]	[12.90]	[1.38]	[−20.24]
5,6-$(C_2H_5)_2$-2,4-$C_2B_5H_5$	−20.59 (176)	5.27 (179)	11.12	11.12	−20.59 (176)
	[−20.85]	[5.78]	[11.55]	[11.55]	[−20.85]
1-Cl-3,5-$(C_2H_5)_2$-2,4-$C_2B_5H_4$	−14.9	15.7	12^b	1^b	−31.1 (777)
	[−14.6]	[16.1]	[12.4]	[0.9]	[−31.6]
1-Cl-3,7-$(C_2H_5)_2$-2,4-$C_2B_5H_4$	−21.8	16^b	1^b	1^b	−21.07
	[−20.9]	[17.4]	[2.7]	[2.7]	[−20.0]
1-Cl-5,6-$(C_2H_5)_2$-2,4-$C_2B_5H_4$	−15.2	7.0^b	11^b	11^b	−31.6
	[−15.2]	[6.9]	[11.1]	[11.1]	[−32.2]
1-Cl-5,7-$(C_2H_5)_2$-2,4-$C_2B_5H_4$	−19.1	8.2 (184)	12.5	1.3	−20.7
	[−21.6]	[8.2]	[12.9]	[1.3]	[−20.6]
3-Cl-1,5-$(C_2H_5)_2$-2,4-$C_2B_5H_4$	−6.8	14.6	12.5^b	0.9	−23.5 (181)
	[5.9]	[15.0]	[12.8]	[1.2]	[−23.8]
3-Cl-1,7-$(C_2H_5)_2$-2,4-$C_2B_5H_4$	−12.6	16^b	3.5^b	3.5^b	−12.6
	[−12.3]	[16.3]	[3.0]	[3.0]	[−12.3]
3-Cl-5,6-$(C_2H_5)_2$-2,4-$C_2B_5H_4$	−17.5 (178)	13.2	10.5	10.5	−17.5 (178)
	[−17.5]	[13.7]	[10.9]	[10.9]	[−17.5]
5-Cl-1,3-$(C_2H_5)_2$-2,4-$C_2B_5H_4$	−7.8*b*	14.1	13^b	1^b	−24.5
	[−7.0]	[14.3]	[13.1]	[0.4]	[−24.9]
5-Cl-1,6-$(C_2H_5)_2$-2,4-$C_2B_5H_4$	-7.8^b	4.5^b	12^b	11^b	−25.2
	[−7.6]	[5.2]	[11.8]	[10.6]	[−25.5]
5-Cl-1,7-$(C_2H_5)_2$-2,4-$C_2B_5H_4$	−14.0	6.6 (180)	13.7	1.5^b	−14.0
	[−14.0]	[6.5]	[13.6]	[0.8]	[−14.0]
5-Cl-3,6-$(C_2H_5)_2$-2,4-$C_2B_5H_4$	−18.7 (170)	13.2^b	10.7^b	10.7^b	−18.7 (170)
	[−18.6]	[13.1]	[11.3]	[10.1]	[−18.6]

[a] All B–H boron resonances observed as doublets and B–X (X = C_2H_5, Cl) borons as singlets. Chemical shifts are relative to $\delta(BF_3{\cdot}Et_2O) = 0$, with negative values upfield; numbers in parentheses are ^{11}B–H coupling constants, in Hz. All experiments data were obtained at 160.44 MHz and/or at 128.34 MHz; for uncertainties in values see Experimental Section and footnote *b* below. Chemical shifts in brackets were calculated by assuming a substituent additivity effect (see text and ref 1, 3, 5, and 6; the "additivity" parameters were obtained by subtracting the 2,4-$C_2B_5H_7$ chemical shifts (see Experimental Section) from the pertinent chemical shifts of the B-monosubstituted system (X = C_2H_5, this study; X = Cl, ref 5). [b] Cannot be accurately determined due to peak overlap.

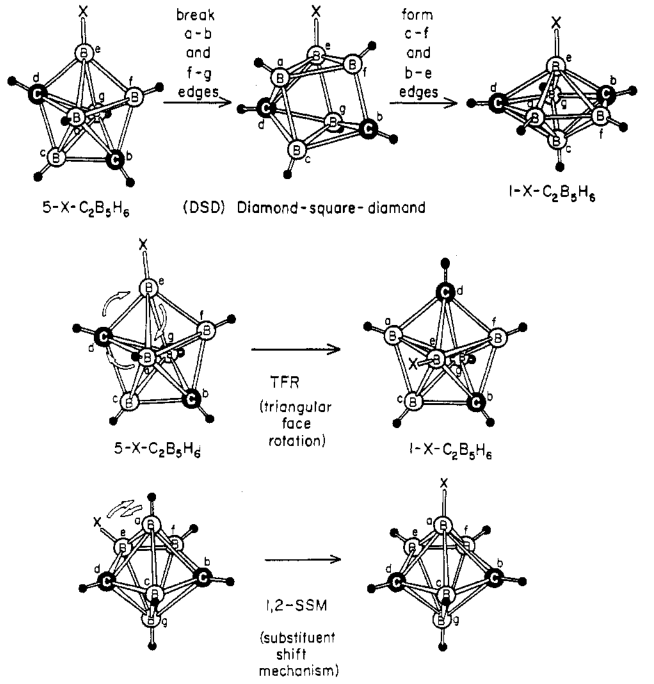


Figure 1. Simple examples of the diamond–square–diamond (DSD), triangular-face-rotation (TFR), and 1,2-substituent-shift mechanisms (SSM) illustrated by the rearrangement of 5-X-*closo*-2,4-$C_2B_5H_6$ to 1-X-*closo*-2,4-$C_2B_5H_6$.

by using a Bruker WP-60 FT spectrometer equipped with a Fluke 6160B boron-11 decoupler operating at 19.25525 MHz in the HC(2,4) and HB(3,5,6) frequency regions and at 19.25485 MHz in the HB(1,7) apex region, and equipped with a General Radio 1062 boron-10 decoupler operating at 6.44785 MHz in the HC(2,4) and HB(3,5,6) frequency regions and 6.447693 MHz in the HB(1,7) apex region; each decoupler was output modulated by a homemade pseudorandom noise generator, which drives an Electronic Navigation Industries Model 3201 power amplifier.

Syntheses of 5-C_2H_5-*closo*-2,4-$C_2B_5H_6$ and 5,6-$(C_2H_5)_2$-*closo*-2,4-$C_2B_5H_5$. Into a 50-mL flask with an attached NMR side tube was sublimed a catalytic amount (ca. 0.2 mmol) of $AlCl_3$. Both $C_2B_5H_7$ (4.0 mmol) and C_2H_5Cl (4.8 mmol) were condensed at −190 °C into the flask; the flask was subsequently sealed and warmed from −190 °C to room temperature. After 164 h at room temperature, a ^{11}B NMR spectrum of the sample indicated that ethylation of $C_2B_5H_7$ had ensued. After the flask and its contents were heated at 81 °C for 3 h, no further change in the ^{11}B NMR was noticed. The flask was opened to the vacuum line, and all volatile materials were subjected to cold-column fractionation; each fraction was subsequently identified by using ^1H and ^{11}B NMR spectroscopic analyses: 0.45 mmol of low molecular weight products (e.g. HCl, BCl_3) vacuum distilled at temperatures below −64 °C; unreacted $C_2B_5H_7$ (2.1 mmol) and C_2H_5Cl (0.3 mmol) distilled between −64 and −46 °C; 5-C_2H_5-2,4-$C_2B_5H_6$ (0.5 mmol) distilled between −46 to −36 °C; and a mixture of 5-C_2H_5-*closo*-2,4-$C_2B_5H_6$ and 5,6-$(C_2H_5)_2$-*closo*-2,4-$C_2B_5H_5$ distilled between −36 and −20 °C. Further separation of this latter mixture by means of cold-column fractionation gave 5,6-$(C_2H_5)_2$-2,4-$C_2B_5H_5$ (0.4 mmol, −26 to −10 °C). See Table I for ^{11}B NMR data for the mono- and diethyl derivatives.

Preparation of 3-Cl-5,6-$(C_2H_5)_2$-*closo*-2,4-$C_2B_5H_4$ from 3-Cl-2,4-$C_2B_5H_6$ and $C_2H_5Cl/AlCl_3$. After a catalytic amount of $AlCl_3$ was sublimed into a 25-mL reaction vessel, 3-Cl-2,4-$C_2B_5H_6$ (1.2 mmol)[11] was added; this was followed by the addition of C_2H_5Cl (1.8 mmol). The

Table II. Kinetic Data for the 295 °C Rearrangement of 5-C_2H_5-*closo*-2,4-$C_2B_5H_6$

total heating time, h	% *B*-C_2H_5-*closo*-2,4-$C_2B_5H_6$ isomers[a]		
	5-C_2H_5-2,4-$C_2B_5H_6$	1-C_2H_5-2,4-$C_2B_5H_6$	3-C_2H_5-2,4-$C_2B_5H_6$
0	99.2	0.8	0.0
4.5	95.7	4.3	0.0
9.6	95.6	4.4	0.0
31.0	92.3	7.7	0.0
109.0	78.2	18.8	3.0
219.0	68.4	26.4	5.2
411.3	55.5	34.5	10.0
688.3	41.3	37.9	20.8
1071.7	32.9	40.4	26.7
1811.0	27.2	38.9	34.4

[a] Average estimated errors in concentration measurements: ±1% for values above 10%; 0.3% for other values.

reaction vessel was sealed and allowed to stand at room temperature for 13 days; the product mixture was passed through −150 and −190 °C traps to remove the side product, HCl. Analysis of the material in the −150 °C trap by ^{11}B NMR showed that the mole percentages of the carboranes 3-Cl-2,4-$C_2B_5H_6$, 3-Cl-5-C_2H_5-2,4-$C_2B_5H_5$, and 3-Cl-5,6-$(C_2H_5)_2$-2,4-$C_2B_5H_4$ were 18%, 47%, and 35%, respectively. The material in the −150 °C trap was further fractionated by cold-column techniques,[12] whereby 3-Cl-5-C_2H_5-2,4-$C_2B_5H_5$ (0.3 mmol) was found to distill between −55 and −35 °C, and 3-Cl-5,6-$(C_2H_5)_2$-2,4-$C_2B_5H_4$ (0.22 mmol) distilled between −30 and 0 °C. For NMR data of 3-Cl-5,6-$(C_2H_5)_2$-2,4-$C_2B_5H_4$ see Table I. For 3-Cl-5-C_2H_5-2,4-$C_2B_5H_5$ the ^{11}B NMR resonances were found at δ (in ppm) = −17.95 (J = 180 Hz) for B(1,7), 14.24 for B(3), 13.0 for B(5), and 0.96 (J = 172.7 Hz) for B(6).

Kinetic Studies on the Rearrangement of 5-C_2H_5-*closo*-2,4-$C_2B_5H_6$, 5,6-$(C_2H_5)_2$-*closo*-2,4-$C_2B_5H_5$, and 3-Cl-5,6-$(C_2H_5)_2$-*closo*-2,4-$C_2B_5H_4$. General Procedures. The kinetics of the substituted carborane thermal rearrangements were followed by monitoring the course of each reaction in a 3-mm NMR tube. This NMR tube was equipped with a 2-mL glass expansion bulb at one end which insured that the rearrangements occurred in the gas phase at 295 °C. The neat substituted carborane was transferred into the NMR tube by the application of conventional vacuum-line techniques; the NMR tube, with its contents, was then sealed and heated at 295 °C for a number of intervals (see Tables II–IV for monoethyl-, diethyl-, and monochlorodiethyl-derivatives of *closo*-2,4-$C_2B_5H_7$, respectively). The thermal rearrangements were carried out in a custom-made metal convection oven (o.d. = 15 in., i.d. = 2 in., length = 30 in.) with fiberglass insulation, and equipped with a temperature control device. The temperature, subject to around-the-clock monitoring, was kept at 295 ± 2 °C for all of the rearrangements.

Proton-decoupled boron spectra were recorded at all time intervals by using a WM-500 FT (160.44 MHz boron-11) spectrometer at the California Institute of Technology regional facility; some resolution-enhanced proton-decoupled boron spectra were also recorded in the search to identify partially overlapping resonances. Proton-coupled ^{11}B and $^{1}H\{^{11}B,^{10}B\}$ spectra were recorded periodically to reinforce peak assignments. The percentages of the isomers present after each heating period were determined by a combination of techniques: (a) normal NMR integration techniques, (b) by weighing peak "cut-outs", and (c) by measuring the peak areas of each boron-11 NMR spectrum with a Lasico model 40 polar compensating planimeter. As part of the procedure to obtain spectra with reliable peak areas, delay times between FID/NMR pulses were increased during the course of taking representative spectra of each of the samples. For example, at various rearrangement time periods the delay times were varied between 0.1 and 1 s with no significant change (within ±1%) observed in area assignments. One of several critical checkpoints in all of these measurements was the area ratio of the total "high-field" region (between δ −6 and −33) to the total "low-field" region (between δ 0 and +17). This area ratio should be close to 2.00:3.00 regardless of the composition, as long as the sample is solely composed of various rearranged *closo*-2,4-$C_2B_5H_7$ derivatives, for the "high-field" region contains all of the apical B(1,7) boron resonances and the "low-field" region contains all of the equatorial B(3,5,6) boron resonances. This measured ratio never departed from the expected 2:3 ratio by more than 1%. Because each isomer within a series exhibited three to five

Table III. Kinetic Data for the Rearrangement of 5,6-$(C_2H_5)_2$-*closo*-2,4-$C_2B_5H_5$ at 295 °C

total heating time, h	% *B,B'*-$(C_2H_5)_2$-2,4-$C_2B_5H_5$ isomers[a]				
	5,6-$(C_2H_5)_2$-	1,5-$(C_2H_5)_2$-	3,5-$(C_2H_5)_2$-	1,3-$(C_2H_5)_i$-	1,7-$(C_2H_5)_2$-
0	90.5	8.0	1.5	0	0
2.0	82.2	15.0	1.8	0	0
6.0	74.2	22.3	3.5	0	0
15.0	54.4	40.5	5.1	0	0
37.0	28.3	54.2	14.5	3.0	0
82.0	11.2	59.0	24.9	4.5	0.4
155.0	5.7	50.7	35.5	7.1	1.0
260.3	4.4	42.8	36.5	12.8	3.5
429.3	4.1	36.9	34.2	19.5	5.3
719.0	3.5	31.8	31.7	25.5	7.5
1269	4.4	30.2	28.9	27.1	9.4

[a] Average estimated errors in concentration measurements: ±1% for values above 10%; 0.3% for other values.

Table IV. Kinetic Data for the Rearrangement of 3-Cl-5,6-$(C_2H_5)_2$-*closo*-2,4-$C_2B_5H_4$ at 295 and 340 °C

total heating time, h	% *B*-Cl-*B′,B″*-$(C_2H_5)_2$-2,4-$C_2B_5H_4$ isomers[a]										
	3-Cl-5,6-Et_2-	1-Cl-5,7-Et_2-	5-Cl-3,6-Et_2-	5-Cl-1,7-Et_2-	3-Cl-1,5-Et_2-	5-Cl-1,3-Et_2-	1-Cl-3,5-Et_2-	5-Cl-1,6-Et_2-	3-Cl-1,7-Et_2-	1-Cl-5,6-Et_2-	1-Cl-3,7-Et_2-
					At 295 °C						
0	98.0	0.0	0.0	0.0	2.0	0.0	0.0	0.0	0.0	0.0	0.0
1.5	92.2	3.6	1.4	0.0	2.8	0.0	0.0	0.0	0.0	0.0	0.0
4.5	91.1	4.4	2.7	0.0	1.8	0.0	0.0	0.0	0.0	0.0	0.0
10.5	77.3	17.5	3.0	0.2	2.0	0.0	0.0	0.0	0.0	0.0	0.0
23	57.7	31.0	4.2	0.2	2.9	0.0	0.0	0.0	0.0	0.0	0.0
48	39.4	43.2	8.9	3.5	3.5	0.9	0.0	0.0	0.6	0.0	0.0
100	24.7	39.3	12.6	10.6	6.4	2.7	1.9	1.1	0.5	0.0	0.0
173	15.9	29.4	17.0	17.2	6.8	5.9	2.3	3.9	0.6	1.2	0.0
311	10.6	20.1	18.9	22.6	9.2	7.1	2.2	3.0	1.9	1.5	2.8
620	5.2	10.0	21.2	23.6	11.7	12.9	4.6	5.8	3.0	0.7	1.3
1233	5.3	8.3	22.7	18.4	11.2	15.5	9.4	4.1	2.9	0.5	2.1
					At 340 °C						
48[b]	1.7	7.4	9.8	6.9	17.0	25.0	12.9	9.6	7.2	1.0	1.2
98[b]	3.2	8.2	7.5	6.9	15.5	26.7	9.1	12.4	8.2	1.0	1.1
312[b]	1.8	6.0	8.3	6.9	16.4	27.6	9.4	12.3	6.9	1.2	3.0

[a] Average estimated errors in concentration measurements: ±1.0% for values above 10%; ±0.5% for values below 10%. [b] Additional heating time.

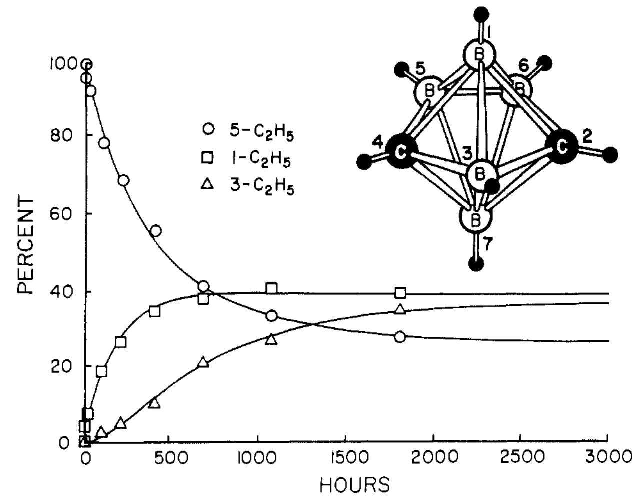


Figure 2. Data (O, □, Δ) for the 295 °C rearrangement of 5-C_2H_5-*closo*-2,4-$C_2B_5H_6$. Curves are fitted to data (Table II) by assuming a DSD mechanism (see text); derived first-order rate constants are given in the Experimental Section.

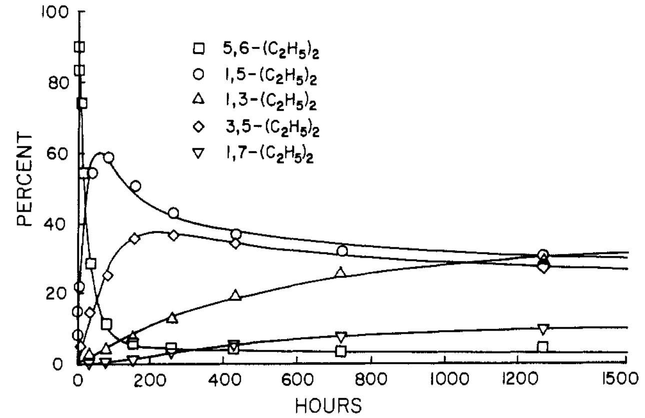


Figure 3. Data (□, O, Δ, ◇, ▽) for the 295 °C rearrangement of 5,6-$(C_2H_5)_2$-*closo*-2,4-$C_2B_5H_5$. Curves are fitted at data (Table III) by assuming a DSD mechanism (see text); derived first-order rate constants are given in the Experimental Section.

Table V. Rearrangement–Equilibrium Data and Calculations for *B*-C_2H_5-, *B,B′*-$(C_2H_5)_2$-, and *B*-Cl-*B′,B″*-$(C_2H_5)_2$- Derivatives of 2,4-$C_2B_5H_7$

compd	% comp at equil (exptl)[a]	W^b	ΔH_{exptl},[c] J	ΔH_{calcd},[d] J	% comp (theor derived from col 3 and 5 and eq 3)[e]
1-C_2H_5-	38.4	2	2968	*f*	*f*
3-C_2H_5-	36.0	1	0	*f*	*f*
5-C_2H_5-	25.6	2	4883	*f*	*f*
1,3-$(C_2H_5)_2$-	33.7	2	0	0	36.2
1,5-$(C_2H_5)_2$i-	28.2	4	4114	4883	25.7
1,7-$(C_2H_5)_2$-	10.0	1	2464	2968	9.7
3,5-$(C_2H_5)_2$-	25.2	2	1372	1915	24.1
5,6-$(C_2H_5)_2$-	2.9	1	8309	6798	4.3
1-Cl-3,5-$(C_2H_5)_2$-	9.4	4	5489	5420	9.3
1-Cl-3,7-$(C_2H_5)_2$-	3.0	2	7777	3505	6.8
1-Cl-5,6-$(C_2H_5)_2$-	1.2	2	12446	10303	1.8
1-Cl-5,7-$(C_2H_5)_2$-	6.0	4	7777	8388	5.2
3-Cl-1,5-$(C_2H_5)_2$-	16.4	4	2652	1915	18.5
3-Cl-1,7-$(C_2H_5)_2$-	6.9	1	0	0	6.7
3-Cl-5,6-$(C_2H_5)_2$-	1.8	1	6848	3830	3.2
5-Cl-1,3-$(C_2H_5)_2$-	27.6	4	0	551	24.2
5-Cl-1,6-$(C_2H_5)_2$-	12.3	4	4119	5434	9.3
5-Cl-1,7-$(C_2H_5)_2$-	6.9	2	3532	3519	6.8
5-Cl-3,6-$(C_2H_5)_2$-	8.3	2	2591	2466	8.3

[a] The carborane isomer equilibrium concentrations, in the mono and diethyl sets were derived from the relevant "best-fit" DSD rate constant ratios; consult text and Figures 2 and 3. These agree well with the data in Tables II and III at long rearrangement times when equilibration appears to have been reached. Estimated errors: ±1.0% for values in the 10–40% range; ±0.5–1.0% for values in the 5–10% range; ±0.3–0.4% for values in the 1–5% range. The equilibrium temperature is 568 K for the mono- and diethyl sets. The isomer equilibrium concentrations for the chlorodiethyl set are taken to be the percentages observed subsequent to the 312-h heating period at 613 K, Table IV (see discussion section for probable errors). [b] *W* is related to the symmetry of the molecule and represents the number of ways a substituent (or substituents) may be placed on the molecule and still represent the same isomer; for a discussion of a related approach see: Benson, S. W. *Thermochemical* Kinetics; Wiley: New York, 1976; p 47. [c] See eq 3 in text; all of the values were derived from relative equilibria concentrations (column 2). The isomer with the lowest enthalpy in each set is arbitrarily assigned $\Delta H = 0$. [d] The diethyl isomer ΔH values are calculated by adding two appropriate monoethyl positional ΔH values from column 4; the isomer in each set with the lowest calculated enthalpy is arbitrarily assigned $\Delta H = 0$. Similarly, the *B*-Cl-*B′,B″*-$(C_2H_5)_2$- ΔH values are calculated by adding three appropriate (one each for the two ethyl groups, column 4, and one for the chloro[5] substituent) positional ΔH values; again the isomer with the lowest ΔH sum is arbitrarily given a base value of zero. [e] The equilibrium percentages calculated for the mono- and diethyl sets are those at 568 K whereas those for the chlorodiethyl isomers are calculated for an equilibrium temperature of 613 K, so that a fair comparison can be made to those values cited in column 2. [f] Not applicable.

peaks, depending on its symmetry, it was possible to have several checkpoint resonance areas for assessing the isomer percentages. Deviations averaged about ±1% for isomers in the 10+% region and averaged ±0.3% for those less than 10%.

Best-fit first-order rate constants were determined by using PROPHET computer programs (DIFFEQ-FITDIFF) made available by Bolt, Berenek, and Newmann through the National Institutes of Health. The best-fit rate constants were subsequently used to generate (by using the DIFFEQ-INTDIFF program) the rate curves shown in Figures 2 and 3 for visual comparison to the measured data.

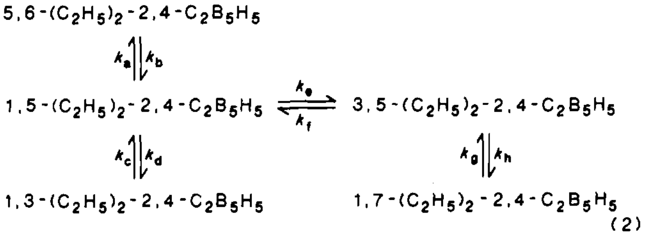
Kinetic Study of the 5-C_2H_5-*closo*-2,4-$C_2B_5H_6$ Thermal Rearrangement. A sample of 5-C_2H_5-2,4-$C_2B_5H_6$ (0.5 mmol), containing 0.8% of 1-C_2H_5-2,4-$C_2B_5H_6$, was sealed in a 3-mm NMR tube equipped with a 2-mL bulb and heated at 295 °C for a number of intervals (Table II). After each heating period the sample was immediately cooled to room temperature and NMR analyses (Table I) of the rearrangement products were made. No significant change in the relative *B*-ethyl isomer concentrations was noted upon heating the sample longer than 1800 h. However, detectable amounts of carborane side-products, which were a combination of *B,B′*-$(C_2H_5)_2$-*closo*-2,4-$C_2B_5H_5$ isomers and some carborane-coupled products were produced toward the termination of the rearrangement.

The kinetic data (Table II) are presented graphically in Figure 2. The first-order diamond–square–diamond (DSD) (see Discussion section) rate constants for eq 1 were determined to be (in 10^{-3} h^{-1}) k_a = 2.00, k_b = 1.34, k_c = 1.50, and k_d = 1.60; a regression analysis, r^2 = 0.995, indicates good agreement between the data points and theoretical isomer percentages generated from use of the fitted rate constants. The equilibrium percentages shown in column 2, Table V, for the three isomers are determined by extending the "best-fit" curves to "time-infinity".

$$\text{5-}C_2H_5\text{-2,4-}C_2B_5H_6 \underset{k_b}{\overset{k_a}{\rightleftharpoons}} \text{1-}C_2H_5\text{-2,4-}C_2B_5H_6 \underset{k_d}{\overset{k_c}{\rightleftharpoons}} \text{3-}C_2H_5\text{-2,4-}C_2B_5H_6 \qquad (1)$$

Kinetic Study of the 5,6-$(C_2H_5)_2$-*closo*-2,4-$C_2B_5H_5$ Thermal Rearrangement. In a manner similar to that described for the rearrangement of 5-C_2H_5-2,4-$C_2B_5H_6$ a sample of 5,6-$(C_2H_5)_2$-2,4-$C_2B_5H_5$ (0.5 mmol), containing 8% 1,5-$(C_2H_5)_2$-2,4-$C_2B_5H_5$ and 1.5% 3,5-$(C_2H_5)_2$-2,4-$C_2B_5H_5$, was heated at 295 °C for a number of intervals (Table III); after each heating period the sample was immediately cooled to room temperature, and NMR analyses of the rearrangement products were made (Table I for ^{11}B NMR chemical shifts and coupling constants). Other carborane species (not identifiable; 7.2% of the total carboranes after a period of 1269 h heating at 295 °C), besides the five *B,B′*-diethylcarborane isomers, were detected in trace amounts as early as the end of 155 h of heating at 295 °C; therefore, the quantities of the *B,B′*-diethylcarborane isomers cited for each heating period in Table III have been normalized to total 100% for all the diethyl species.

The best-fit first-order rate constants were determined for a rearrangement pathway, eq 2, based on the diamond–square–diamond (DSD) mechanism (vide infra), and the kinetic data (Table III) are presented graphically in Figure 3. The derived rate constants are (in 10^{-3} h^{-1}) k_a = 3.55, k_b = 34.0, k_c = 0.987, k_d = 1.18, k_e = 8.44, k_f = 9.46, k_g = 1.29, and k_h = 0.513; a regression analysis, r^2 = 0.997, indicates good agreement between the data points and theoretical isomer percentages generated from use of the fitted rate constants. The equilibrium percentages shown in column 2, Table V, for the five isomers are determined by extending the "best-fit" curves to "time-infinity".



(2)

Kinetic Study of the 3-Cl-5,6-$(C_2H_5)_2$-*closo*-2,4-$C_2B_5H_4$ Thermal Rearrangement. A quantity of 3-Cl-5,6-$(C_2H_5)_2$-$C_2B_5H_4$ (0.22 mmol), containing 2% of 3-Cl-1,5-$(C_2H_5)_2$-$C_2B_5H_4$, was heated at 295 °C for various time intervals (Table IV). After each heating period the rearrangement process was essentially quenched by cooling the sample immediately to room temperature, and an NMR analysis (Table I) of the monochlorodiethylcarborane rearrangement products was made. The results are presented graphically in Figure 4. After 1233 h at 295 °C the rearrangement was proceeding too slowly for efficient analysis, and therefore the temperature was raised to 340 °C for further heating intervals. During the higher temperature heating periods a number of side products were gradually building up, and by the end of the 312 h, 340 °C heating period, it was becoming difficult to assign reasonably accurate percentages to the *B*-Cl-*B*,*B'*-$(C_2H_5)_2$-*closo*-2,4-$C_2B_5H_4$ rearrangement products. The rearrangement was then terminated.

Results and Discussion

The ethylation of both *closo*-2,4-$C_2B_5H_7$ and its 3-chloro derivative, using $C_2H_5Cl/AlCl_3$ as the reagent mixture, results in initial attack at the 5-position and subsequent attack at the related equatorial 6-position. Minor amounts of 1,5-diethyl products are obtained in both cases. The general course of these reactions parallels, as might well be expected, the methylation of this same carborane system.[1,2,14]

Thermal equilibration of the 5-C_2H_5-2,4-$C_2B_5H_6$ with the two other *B*-ethyl isomers (1-C_2H_5- and 3-C_2H_5-) in this carborane system is nearly complete after 1800 h at 295 °C (Table II, Figure 2). The relative amounts of each of the isomers observed under these conditions initially suggest that the 1-C_2H_5- isomer is the most stable of the three, but a statistical correction that takes into account equivalent cage positions (i.e., in the parent carborane: 5-position = 6-position, 1-position = 7-position, and the 3-position is unique) leads to the cage positional preference for a *B*-C_2H_5 group: 3- > 1- > 5-. This order of substituent positional preference is essentially the same as that found for the *B*-methyl carboranes;[1-3] however, the DSD rearrangement rate constants of the ethyl system (see Experimental Section) are 3–5 times smaller than the corresponding DSD pattern rate constants for the methyl system.[2,3]

Rearrangement of the 5,6-$(C_2H_5)_2$-*closo*-2,4-$C_2B_5H_5$ isomer to give a mixture of all five *B*,*B'*-$(C_2H_5)_2$-2,4-$C_2B_5H_5$ isomers proceeds at a reasonable rate at 295 °C; the 1,5-$(C_2H_5)_2$-2,4-$C_2B_5H_5$ isomer is produced initially (Table III, Figure 3), followed by the buildup of 3,5-$(C_2H_5)_2$-, 1,3-$(C_2H_5)_2$-, and finally the 1,7-$(C_2H_5)_2$-2,4-$C_2B_5H_5$ isomers. After the *B*,*B'*-diethyl isomers are allowed to reach equilibrium, it is noted that the relative isomer stabilities are as follows: 1,3- > 1,5- > 3,5- > 1,7- > 5,6-$(C_2H_5)_2$-2,4-$C_2B_5H_5$. When statistically corrected (e.g. "four" compounds, 1,5-, 1,6-, 5,7-, and 6,7-$(C_2H_5)_2$-2,4-$C_2B_5H_5$ make up the 1,5-isomer set, but there is only "one" 5,6-$(C_2H_5)_2$-2,4-$C_2B_5H_5$, etc.), the isomer stabilities are 1,3- > 3,5- > 1,7- > 1,5- > 5,6-$(C_2H_5)_2$-2,4-$C_2B_5H_5$. The order of diethyl isomer stabilities is the same as that of dimethyl isomer stabilities;[1,3] however, the rearrangement DSD pattern rate constants for the diethyl system (see Experimental Section) are 1.8–4.6 times slower than the corresponding rate constants for the dimethyl system.[3]

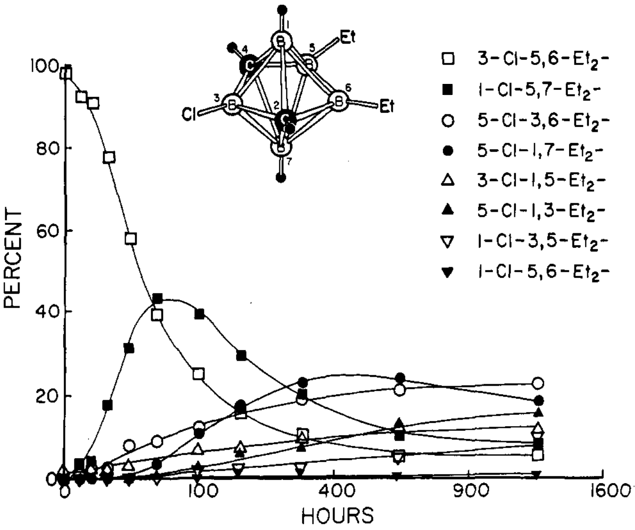


Figure 4. Data, with best-fit curves, for the 295 °C rearrangement of 3-Cl-5,6-$(C_2H_5)_2$-*closo*-2,4-$C_2B_5H_4$. For clarity, curves for only 8 of the 11 isomers are shown here. In order to plot the heating intervals in a reasonable fashion, it was found expedient to make the division spacings along the horizontal axis follow the relationship: distance along axis is proportional to the square root of the time.

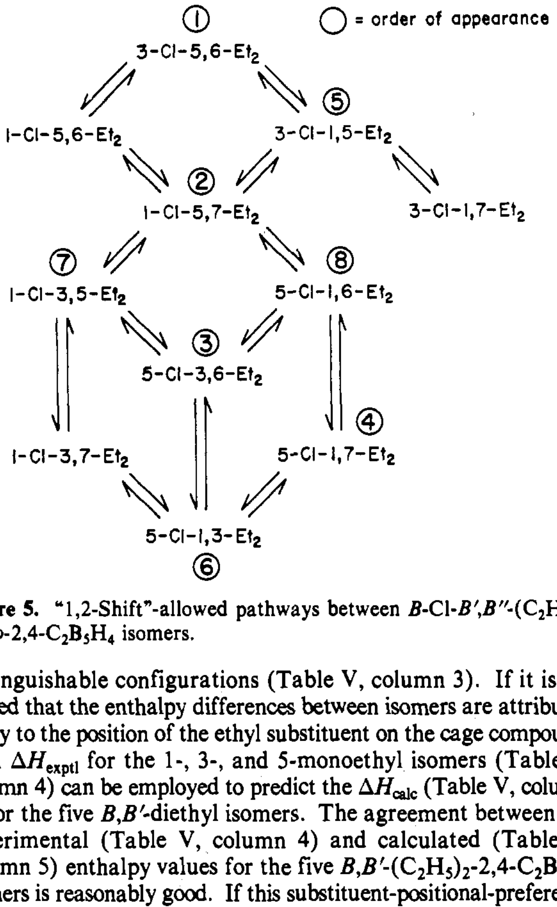


Figure 5. "1,2-Shift"-allowed pathways between *B*-Cl-*B'*,*B''*-$(C_2H_5)_2$-*closo*-2,4-$C_2B_5H_4$ isomers.

Enthalpy differences (Table V, column 4) among monoethyl and diethyl isomers can be obtained from the experimental percent isomer data (Table V, column 2) by utilizing the relationship

$$\Delta H = -RT \ln K + T\Delta(R \ln W) \qquad (3)$$

where $R \ln W$ is the molar enthalpy and W is the number of distinguishable configurations (Table V, column 3). If it is assumed that the enthalpy differences between isomers are attributed solely to the position of the ethyl substituent on the cage compound, then ΔH_{exptl} for the 1-, 3-, and 5-monoethyl isomers (Table V, column 4) can be employed to predict the ΔH_{calc} (Table V, column 5) for the five *B*,*B'*-diethyl isomers. The agreement between the experimental (Table V, column 4) and calculated (Table V, column 5) enthalpy values for the five *B*,*B'*-$(C_2H_5)_2$-2,4-$C_2B_5H_5$ isomers is reasonably good. If this substituent-positional-preference ΔH additivity effect[1,3,5,6] is coupled with eq 3, equilibrium quantities (Table V, column 6) of the *B*,*B'*-diethyl compounds can be predicted from the experimental *B*-monoethylcarborane equilibrium results. The stability order of all the *B*,*B'*-diethylcarborane isomers is correctly forecasted in this fashion in that the predicted isomer equilibrium quantities (Table V, column 6) compare favorably with the experimentally observed percentages (Table V, column 2). However, it should be noted that the estimated stabilities from the utilization of a ΔH additivity argument overestimates the stability of the 5,6-diethyl isomer at the expense of the other isomers. An examination of molecular models indicates that the most serious steric problem within the

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(14) Ditter, J. F.; Klusmann, E. B.; Williams, R. E.; Onak, T. *Inorg. Chem.* **1976**, *15*, 1063–1065.

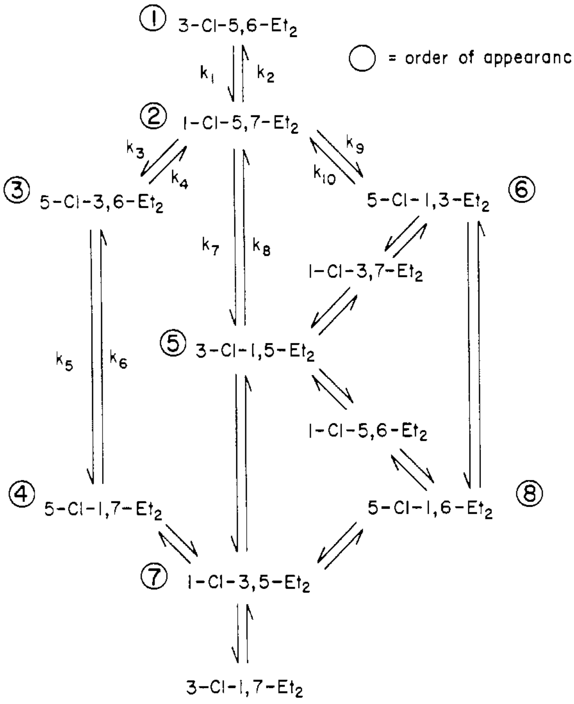

Figure 6. DSD-allowed pathways (with cage carbon movement restrictions; see text) between B-Cl-B',B''-$(C_2H_5)_2$-*closo*-2,4-$C_2B_5H_4$ isomers. Approximate rate constants for k_1–k_{10} (in 10^{-3} h^{-1}): k_1 = 24, k_2 = 11, k_3 = 8, k_4 = 5, k_5 = 32, k_6 = 31, k_7 = 1, k_8 = 0.3, k_9 = 1, k_{10} = 0.2.

collection of diethyl isomers is to be found in the 5,6-diethyl system, and therefore, it is not totally surprising to find that this isomer is experimentally found to be less stable than predicted.

The first B-Cl-B',B''-$(C_2H_5)_2$-*closo*-2,4-$C_2B_5H_4$ isomer that is produced during the thermal rearrangement of 3-Cl-5,6-$(C_2H_5)_2$-*closo*-2,4-$C_2B_5H_4$ is 1-Cl-5,7-$(C_2H_5)_2$-*closo*-2,4-$C_2B_5H_4$ (Table IV, Figure 4). Should a 1,2-substituent-shift mechanism[10] be operating (see Figures 1 and 5) this result is unexpected; however, this experimental observation is consistent with a DSD[7–9,15] pathway (Figures 1 and 6). Moreover, the next isomer, 5-Cl-3,6-$(C_2H_5)_2$-*closo*-2,4-$C_2B_5H_4$, making an appearance during the course of the rearrangement, cannot be directly produced from either the initial 3-Cl-5,6-$(C_2H_5)_2$- or 1-Cl-5,7-$(C_2H_5)_2$- isomers via the 1,2-shift mechanism (Figure 5) but is fully expected from the latter isomer via a DSD scheme (Figure 6). Either (or both) of two conditions that would allow the 1,2-shift mechanism to be ruled out are as follows: (a) At the time the 1-Cl-5,7-$(C_2H_5)_2$- isomer is produced neither 1-Cl-5,6-$(C_2H_5)_2$- and/or 3-Cl-1,5-$(C_2H_5)_2$- isomers are present in quantities greater than at the start of the reaction. And importantly, the latter two isomers should be produced later; otherwise, it could be argued that these isomers could be fleeting intermediates at the start of the rearrangement. (b) At the time the 5-Cl-3,6-$(C_2H_5)_2$- isomer is produced neither the 1-Cl-3,5-$(C_2H_5)_2$- nor 5-Cl-1,6-$(C_2H_5)_2$- isomer(s) are formed, but they should be found later in the rearrangement. Because the 1-Cl-5,6-$(C_2H_5)_2$- isomer is never observed in a quantity much above 1%, it is not clear that the specified requirement(s) of consideration a can be totally met. The experimental observations throughout the rearrangement (Table IV), however, do meet the requirements of consideration b. Therefore, the 1,2-shift mechanism can be decisively ruled out.

It is noted that a triangle-face-rotation (TFR) mechanism[8,10] has been previously ruled out for the B-CH_3- and B-$ClC_2B_5H_6$ thermal rearrangements,[2,3,5] and in the present work, the rearrangement pattern for B-Cl-B',B''-$(C_2H_5)_2$-*closo*-2,4-$C_2B_5H_4$ is consistent with this conclusion (see Figures 1 and 7).

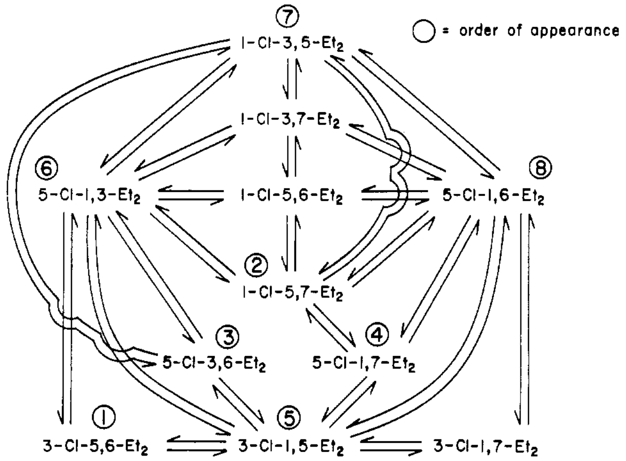

Figure 7. TFR-allowed pathways (with cage carbon movement restrictions; see text) between B-Cl-B',B''-$(C_2H_5)_2$-*closo*-2,4-$C_2B_5H_4$ isomers.

The formation of "side products" toward the termination of the B-Cl-B',B''-$(C_2H_5)_2$-*closo*-2,4-$C_2B_5H_4$ rearrangement (see Experimental Section) makes it next to impossible to obtain reliable final equilibrium data and thus difficult to calculate accurate unimolecular rate constants for the DSD scheme in Figure 6. It is observed, however, that the isomer percentages at the last 340 °C heating period are nearly the same, in most cases, as those expected from application of a positional additivity effect (cf. column 2 with column 6 of Table V). This makes it highly probable that the monochlorodiethylcarborane rearrangement was not far from equilibrium when it was stopped. Enthalpy calculations similar to those above for the mono- and diethyl systems (see also Table V, column 4) give the following order of isomer stabilities for B-Cl-B',B''-$(C_2H_5)_2$-*closo*-2,4-$C_2B_5H_4$:

3-Cl-1,7-Et_2- = 5-Cl-1,3-Et_2- > 5-Cl-3,6-Et_2- >
3-Cl-1,5-Et_2-> 5-Cl-1,7-Et_2- >
5-Cl-1,6-Et_2- >1-Cl-3,5-Et_2- > 3-Cl-5,6-Et_2- >
1-Cl-3,7-Et_2- = 1-Cl-5,7-Et_2- > 1-Cl-5,6-Et_2-

Considering the problems in obtaining a reliable equilibration between the isomers, the agreement between the above estimated isomer (experimental) stability order and the stability order predicted by the enthalpy additivity argument (Table V, column 5, and above discussion)

3-Cl-1,7-Et_2- > 5-Cl-1,3-Et_2- > 3-Cl-1,5-Et_2- >
5-Cl-3,6-Et_2- > 1-Cl-3,7-Et_2- > 5-Cl-1,7-Et_2- >
3-Cl-5,6-Et_2- > 1-Cl-3,5-Et_2- > 5-Cl-1,6-Et_2- >
1-Cl-5,7-Et_2- > 1-Cl-5,6-Et_2-

is rather good for the isomers at the extreme ends and less good for those with apparent intermediate stabilities. When the diethyl enthalpy differences, instead of the monoethyl enthalpy differences, are used for the calculation of the chlorodiethyl values in column 5 of Table V, the following stability order is obtained:

3-Cl-1,7-Et_2- > 5-Cl-1,3-Et_2- > 3-Cl-1,5-Et_2- >
5-Cl-3,6-Et_2- > 5-Cl-1,7-Et_2- > 1-Cl-3,7-Et_2- >
5-Cl-1,6-Et_2- > 1-Cl-3,5-Et_2- > 3-Cl-5,6-Et_2- >
1-Cl-5,7-Et_2- > 1-Cl-5,6-Et_2-

This is a better fit to the experimental estimate of the relative stabilities with the most notable exception being that of the 1-Cl-3,7-Et_2- isomer. This better fit may be a reflection of the diethyl steric problem cited earlier in this discussion section.

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Contribution from Rocketdyne, A Division of Rockwell International,
Canoga Park, California 91303

Reactions of Chlorine Fluorides and Oxyfluorides with the Nitrate Anion and Alkali-Metal Fluoride Catalyzed Decomposition of ClF_5

Karl O. Christe,* William W. Wilson, and Richard D. Wilson

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The binary chlorine fluorides ClF_5, ClF_3, and ClF, when used in an excess, all undergo facile fluorine–oxygen exchange reactions with the nitrate anion, forming $FClO_2$, unstable FClO, and $ClONO_2$, respectively, as the primary products. Whereas $FClO_3$ does not react with $LiNO_3$ at temperatures as high as 75 °C, $FClO_2$ readily reacts with either $LiNO_3$ or N_2O_5 to give $ClONO_2$ and O_2 in high yield, probably via the formation of an unstable O_2ClONO_2 intermediate. With an excess of ClF, chlorine nitrate undergoes a slow reaction to give FNO_2 and Cl_2O as the primary products, followed by Cl_2O reacting with ClF to give Cl_2, ClF, and $FClO_2$. The alkali-metal fluorides CsF, RbF, and KF catalyze the decomposition of ClF_5 to ClF_3 and F_2, which can result in the generation of substantial F_2 pressures at temperatures as low as 25 °C.

Introduction

Ionic nitrates are surprisingly reactive toward the fluorides and oxyfluorides of bromine,[1,2] xenon,[3,4] and iodine.[5] The observed reaction chemistry is fascinating and often unpredictable. Thus, BrF_5 undergoes fluorine–oxygen exchange reactions that, depending on the choice of the nitrate salt or the reagent used in excess, yield either BrF_4O^- salts, free BrF_3O, or bromine nitrates. In the cases of XeF_6, $XeOF_4$, and IF_5, stepwise fluorine–oxygen exchange occurs, whereas for the closely related IF_7 molecule, reduction to IF_5 with simultaneous oxygen evolution was observed. In view of these results it was interesting to study the behavior of chlorine fluorides and oxyfluorides toward ionic nitrates.

The previous reports on reactions of ionic nitrates with chlorine fluorides are limited to a statement by Ruff and Krug that KNO_3 does not react with liquid ClF_3 while $AgNO_3$ does[6] and a synthesis of $ClONO_2$ from ClF and $M(NO_3)_2$ where M is either Ca, Sr, Ba, or Pb.[7] In addition, the reactions of ClF,[8,9] ClF_3,[9] ClF_5,[9] and $FClO_2$[9] with the covalent nitrate $HONO_2$ have previously been studied.

Experimental Section

Apparatus and Materials. The vacuum lines, handling techniques, and spectrometers used in this study have been described elsewhere.[3] Commercial $LiNO_3$ (J. T. Baker, 99.7%), $NaNO_3$ (J. T. Baker, 99.5%), KNO_3 (J. T. Baker, 99.1%), and $RbNO_3$ (K&K Labs, Inc., 99.9%) were dried in vacuo at 120 °C for 1 day prior to their use. $CsNO_3$ was prepared from Cs_2CO_3 and HNO_3 and dried in the same manner. N_2O_5,[10] ClF_5,[11] ClF,[12] and $FClO_2$[13] were prepared by literature methods. $FClO_3$ (Pennsalt) and ClF_3 (Matheson) were commercial materials and were purified by fractional condensation prior to their use.

Caution! Chlorine fluorides and oxyfluorides are powerful oxidizers and can react violently with most organic substances. The materials should be handled only in well-passivated metal–Teflon equipment with all the necessary safety precautions.

Reaction of ClF with an Excess of $NaNO_3$. A mixture of $NaNO_3$ (17.32 mmol) and ClF (11.53 mmol) in a 30-mL stainless steel cylinder was allowed to slowly warm in a dry ice–liquid N_2 slush bath from −196 to −78 °C and then toward 0 °C. The cylinder was recooled to −196 °C and did not contain any gas noncondensible at this temperature. The material volatile at room temperature was separated on warm up of the cylinder from −196 °C by fractional condensation through traps kept at −112, −126, −142, and −196 °C. The −112 °C trap contained $ClONO_2$[14] (8.89 mmol) and Cl_2O[15] (0.68 mmol), the one at −126 °C had $ClONO_2$ (0.09 mmol), the one at −142 °C had Cl_2 (0.35 mmol), while the one at −196 °C contained FNO_2[16] (1.01 mmol). The white solid residue in the cylinder was a mixture of NaF and $NaNO_3$ (1046 mg; weight calculated for 9.99 mmol of NaF and 7.33 mmol of $NaNO_3$ = 1043 mg). The yield of $ClONO_2$, based on ClF, was 76%.

Reaction of $NaNO_3$ with an Excess of ClF. Finely powdered $NaNO_3$ (5.15 mmol) was loaded in the drybox into a prepassivated 30-mL stainless steel cylinder equipped with a valve. On the vacuum line, ClF (8.00 mmol) was added at −196 °C. The cylinder was allowed to slowly warm to room temperature, where it was kept for 3 days. It was cooled again to −196 °C and did not contain any gas noncondensible at this temperature. The material volatile at room temperature was separated on warm up of the cylinder from −196 °C by fractional condensation through traps kept at −142 and −196 °C. The −196 °C trap contained FNO_2 (2.88 mmol) and the one at −142 °C had 5.14 mmol of a mixture

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