

Synthetic and Rearrangement Studies on the Carboranes $B-X-closo-2,4-C_2B_5H_6$ and $B,B'-X_2-closo-2,4-C_2B_5H_5$ ($X = Br, I$). Correlation of B -Halo- and B,B' -Dihalodicarba- $closo$ -heptaborane Isomer Stabilities¹

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Synthetic routes to all of the $B-X-closo-2,4-C_2B_5H_6$ and $B,B'-X_2-closo-2,4-C_2B_5H_5$ ($X = Br, I$) isomers, with the exception of 1,7- $Br_2-2,4-C_2B_5H_5$, are reported. Reaction of I_2 with $C_2B_5H_7$ in the presence of a Lewis acid gives apparent initial halogen attack at the cage 5-position, whereas the same reaction in the absence of the Lewis acid gives 3- $I-2,4-C_2B_5H_6$ as the initial product. Rearrangements of 5- $Br-$ and 5- $I-2,4-C_2B_5H_6$ to equilibrium quantities of the other related $B-X-closo-2,4-C_2B_5H_6$ isomers take place at a reasonable rate at 295 °C. The thermal rearrangements of the corresponding 5,6- $X_2-closo-2,4-C_2B_5H_5$ compounds to give equilibrium amounts of all five $B,B'-X_2-closo-2,4-C_2B_5H_5$ ($X = Br, I$) isomers are, at the outset of the rearrangement, significantly faster than the 5-monohalodicarbaheptaborane rearrangements. From isomer equilibrium measurements the stabilities of the B -monobromo isomers follow the order (after statistical corrections) 3- $Br-$ > 5- $Br-$ > 1- $Br-2,4-C_2B_5H_6$ whereas the stability order for the B -iodo isomers is 5- $I-$ > 3- $I-$ > 1- $I-2,4-C_2B_5H_6$. The trends in isomer stabilities (with statistical corrections) for the $B,B'-X_2-closo-2,4-C_2B_5H_5$ systems are 3,5- > 5,6- > 1,3- > 1,5- > 1,7-isomer for $X = Br$ and 5,6- > 3,5- > 1,5- > 1,3- > 1,7-isomer for $X = I$. Isomer stabilities within the bromo and iodo systems are compared with those previously reported for the chlorocarborane analogues, and the equilibrium quantities of the dibromo- and diiodocarboranes are interrelated to those for the corresponding monosubstituted compounds. Substituent effects on the boron-11 NMR chemical shifts are correlated among the known fluoro, chloro, bromo, and iodo derivatives of 2,4- $C_2B_5H_7$.

Introduction

Known B -halogen derivatives of the pentagonal-bipyramidal 2,4- $C_2B_5H_7$ are as follows: 1-, 3-, and 5- $F-C_2B_5H_6$,² the three corresponding monochloro derivatives,³⁻⁵ one B -bromo (the 5-isomer) compound,⁶ three of the five possible $B,B'-F_2-closo-2,4-C_2B_5H_5$ isomers,² all five of the $B,B'-Cl_2-closo-2,4-C_2B_5H_5$ isomers,^{3,5} and evidence of some trichloro, tetrachloro, and the per- B -pentachloro derivatives.⁵ One of the objects of the present study, to synthesize and characterize the two remaining mono- B -bromo derivatives and all possible $B,B'-Br_2$, $B-I$, and $B,B'-I_2$ isomers of this carborane system, was realized with one exception, the 1,7- Br_2 derivative.

The relative stabilities of B -monomethyl- and B,B' -dimethyl-dicarbaheptaboranes^{7,8} as well as the B -monochloro- and B,B' -dichlorodicarbaheptaboranes^{3,5} have been determined from thermal rearrangement-equilibration studies. Analogous rearrangement studies on the monobromo, dibromo, monoiodo, and diiodo derivatives of $closo-2,4-C_2B_5H_7$ are reported in the present work, and the results are compared to those found for the methyl and chloro compounds. Of particular interest are cage-positional-preference differences among the halogens in proceeding from chloro- to bromo- to iododicarbaheptaboranes, and how these preference patterns correlate with the nature of each halogen.

Experimental Section

Materials and Handling of Chemicals. The parent $closo-2,4-C_2B_5H_7$ was obtained from R. E. Williams, Chemical Systems Inc., Irvine, CA. Aluminum chloride, obtained from both Spectrum Chemical Corp. and Aldrich Chemical Corp., was freshly sublimed directly into the reaction vessel(s) prior to use. Liquid bromine was dried over molecular sieves prior to use. n -Pentane, obtained from J. T. Baker Chemical Co., and iodine, obtained from Fisher Scientific Co., were used as received.

- (1) The compounds reported in the present work have been named, and numbered, by using previously accepted nomenclature rules. It is noted, however, that a new nomenclature scheme has been devised for cage polyboranes; e.g., 5-(iodo)hexahydro-2,4-dicarba[$D_{5h}-(1\sigma^5 5\sigma^4 1\sigma^3)-\Delta^{10}$ - $closo$]heptaborane is recommended for 5- $I-closo-2,4-C_2B_5H_6$: (a) Casey, J. B.; Evans, W. J.; Powell, W. H. *Inorg. Chem.* **1983**, *22*, 2236-2245. (b) *Ibid.* **1983**, *22*, 2228-2235. (c) *Ibid.* **1981**, *20*, 3556-3561. (d) *Ibid.* **1981**, *20*, 1333-1341.
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Nuclear Magnetic Resonance. Boron-11 NMR spectra were obtained by using both Varian HA-100 CW (32.1 MHz) and Bruker WM-500 FT (160.44 MHz) spectrometers. Proton-decoupled boron spectra were also recorded at all B -halo- and B,B' -dihalocarborane rearrangement time intervals (see below). By varying the delay times between FID pulses, saturation effects were minimized in the determination of rearrangement mixture isomer concentrations by NMR area measurements. The boron chemical shift data (Table I) were referenced relative to $BF_3 \cdot Et_2O$, $\delta = 0.00$, with the parent 2,4- $C_2B_5H_7$ used as a secondary standard: $\delta(1,7) = -21.73$ ppm, $J(^{11}BH) = 180$ Hz; $\delta(3) = +7.02$ ppm $J = 183$ Hz; $\delta(5,6) = +3.83$ ppm, $J = 170$ Hz. Negative chemical shift values are upfield of the $BF_3 \cdot Et_2O$ resonance. Approximate chemical shift and coupling constant errors for all dicarbaheptaboranes (parent and derivatives) are as follows: ± 0.02 ppm, ± 3 Hz, for the cage 1,3- and 7-positions of the carborane; ± 0.06 ppm, ± 10 Hz, for the cage 5- and 6-positions.

Triple-resonance proton NMR spectra (60 MHz) were obtained on a Bruker WP-60 FT spectrometer equipped with a Fluke 6160B frequency synthesizer set at 19.255 MHz for decoupling boron-11 and a Fluke 6011A frequency synthesizer set at 6.447 MHz for decoupling boron-10; the frequency synthesizers were powered by ENI Model 320L RD amplifiers.

Bromination of $C_2B_5H_7$. A mixture of $C_2B_5H_7$ (0.5 mmol) and Br_2 (0.25 mmol) was sealed in an NMR tube and allowed to stand at room temperature for a total of 131 days. During this time period the contents of the tube were periodically monitored by ^{11}B NMR; slow formation of 5- $BrC_2B_5H_6$ was observed, and at the end of the 131-day period a ratio of 1:2 5- $BrC_2B_5H_6/C_2B_5H_7$ was present in the NMR tube. After the sample was heated for 20 h at 140 °C, and subsequently for 26 h at 170 °C, a ratio of 1:1.2 5- $BrC_2B_5H_6/C_2B_5H_7$ was present (as assessed by ^{11}B NMR) in the sample tube. Two larger scale reaction mixtures were prepared, consisting of 5 mmol of $C_2B_5H_7$ and 7.5 mmol of bromine, and 5 mmol of $C_2B_5H_7$ and 15 mmol of bromine, respectively. Both samples were treated at 170 °C for 24 h and subsequently at 200 °C for another 24 h. Both heated samples showed, by ^{11}B NMR analysis, product mixtures of 5- $Br-2,4-C_2B_5H_6$, 5,6- $Br_2-2,4-C_2B_5H_5$, BBr_3 , and only a trace of the parent $C_2B_5H_7$ starting material. The products of the two reaction containers were combined and fractionated through traps at -15 °C (ca. 1.5 mmol 5,6- $Br_2-C_2B_5H_5$), -63 °C (ca. 4.5 mmol 5- $Br-C_2B_5H_6$ and ca. 9 mmol BBr_3 , $\delta(^{11}B) = +38.5$ s),⁹ -130 °C ($C_2B_5H_7$), and -190 °C (HBr). Separation of BBr_3 from 5- $Br-C_2B_5H_6$ was accomplished by cold-column fractionation,¹⁰ with the 5- $Br-C_2B_5H_6$ emerging from the column at -60 to -70 °C.

Iodination of $C_2B_5H_7$ in the Presence of $AlCl_3$. A quantity of $C_2B_5H_7$ (3.0 mmol) was combined with I_2 (1.6 mmol), $AlCl_3$ (ca. 7 mg), and n -pentane (2 mL) in a 25-mL glass reaction vessel. The vessel, with its contents, was sealed and subjected to a temperature of 90 °C for 26 h. Cold-column separation of the vessel's contents gave the following fractions: -97 to -86 °C, ca. 1 mmol pentane; -86 to -80 °C, mostly pentane

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Table I. ^{11}B NMR Data for Various Bromo and Iodo Derivatives of $2,4\text{-C}_2\text{B}_5\text{H}_7^a$

compd	atom				
	B(1)	B(3)	B(5)	B(6)	B(7)
1-Br-2,4- $\text{C}_2\text{B}_5\text{H}_6$	-22.44	8.19 (200)	4.16 (177)	4.16 (177)	-29.87 (184)
3-Br-2,4- $\text{C}_2\text{B}_5\text{H}_6$	-18.06 (185)	10.04	4.16 (177)	4.16 (177)	-18.06 (185)
5-Br-2,4- $\text{C}_2\text{B}_5\text{H}_6$	-19.82 (185)	6.10 (189)	8.64	2.74 (174)	-19.82 (185)
1,3-Br ₂ -2,4- $\text{C}_2\text{B}_5\text{H}_5$	-18.89	11.07	4.32 (~180)	4.32 (~180)	-26.20 (196)
	[-18.77]	[11.21]	[4.49]	[4.49]	[-26.20]
1,5-Br ₂ -2,4- $\text{C}_2\text{B}_5\text{H}_5$	-20.41	7.72 (~190)	8.53	2.43 (177)	-27.76 (192)
	[-20.53]	[7.27]	[8.97]	[3.07]	[-27.96]
3,5-Br ₂ -2,4- $\text{C}_2\text{B}_5\text{H}_5$	-16.32 (192)	8.53	8.53	2.43 (177)	-16.32 (192)
	[-16.59]	[9.12]	[8.97]	[3.07]	[-16.15]
5,6-Br ₂ -2,4- $\text{C}_2\text{B}_5\text{H}_5$	-18.00 (188)	4.58 (195)	6.66	6.66	-18.00 (188)
	[-17.91]	[5.18]	[7.55]	[7.55]	[-17.91]
1-I-2,4- $\text{C}_2\text{B}_5\text{H}_6$	-39.57	8.41 (209)	4.57 (~180)	4.57 (~180)	-24.53 (189)
3-I-2,4- $\text{C}_2\text{B}_5\text{H}_6$	-18.15 (182)	-4.59	5.30 (173)	5.30 (173)	-18.15 (182)
5-I-2,4- $\text{C}_2\text{B}_5\text{H}_6$	-20.22 (185)	7.09 (189)	-7.57	4.25 (176)	-20.22 (185)
1,3-I ₂ -2,4- $\text{C}_2\text{B}_5\text{H}_5$	-34.90	-2.00	6.08 (190)	6.08 (190)	-20.20 (~180)
	[-35.99]	[-3.20]	[6.04]	[6.04]	[-20.95]
1,5-I ₂ -2,4- $\text{C}_2\text{B}_5\text{H}_5$	-36.36	9.00 (207)	-7.00	5.80 (190)	-22.64 (196)
	[-38.06]	[8.48]	[-6.83]	[4.99]	[-23.02]
3,5-I ₂ -2,4- $\text{C}_2\text{B}_5\text{H}_5$	-16.30 (186)	-5.27	-5.70	6.08 (190)	-16.30 (186)
	[-16.64]	[-4.52]	[-6.10]	[5.72]	[-16.64]
5,6-I ₂ -2,4- $\text{C}_2\text{B}_5\text{H}_5$	-18.08 (188)	7.57 (202)	-5.27	-5.27	-18.08 (188)
	[-18.71]	[7.16]	[-7.15]	[-7.15]	[-18.71]

^a All B-H boron resonances are observed as doublets and B-X (X = Br, I) borons as singlets. Chemical shifts are in ppm relative to $\delta(\text{BF}_3 \cdot \text{Et}_2\text{O}) = 0$, with negative values upfield; numbers in parentheses are ^{11}B -H coupling constants, in Hz. All experimental data were obtained at 160.44 MHz. Chemical shifts in brackets are calculated assuming a substituent additivity effect (see text).

Table II. Kinetic Data for the Rearrangement of 5-Br-*closo*-2,4- $\text{C}_2\text{B}_5\text{H}_6$ at 295 °C

total heating time, h	% B-Br- <i>closo</i> -2,4- $\text{C}_2\text{B}_5\text{H}_6$ isomers ^a		
	5-Br $\text{C}_2\text{B}_5\text{H}_6$	1-Br $\text{C}_2\text{B}_5\text{H}_6$	3-Br $\text{C}_2\text{B}_5\text{H}_6$
0	100.0	0.0	0.0
24	89.6	4.7	5.7
168	75.9	10.6	13.5
288	69.9	14.1	15.9
432	61.9	15.8	22.3
888	54.5	17.1	28.3
1488	50.2	17.8	31.9
2017	49.6	17.3	33.1

^a Average estimated errors in concentration measurements: $\pm 1\%$.

(ca. 18 mmol) and a trace quantity of $\text{C}_2\text{B}_5\text{H}_7$; -80 to -75 °C, a fraction (0.5 mmol) consisting mostly of the parent $\text{C}_2\text{B}_5\text{H}_7$; room temperature, a fraction containing pure 5-I-2,4- $\text{C}_2\text{B}_5\text{H}_6$ (1.25 mmol). A nonvolatile fraction, 5,6-I₂-2,4- $\text{C}_2\text{B}_5\text{H}_5$ (0.2 mmol), was removed from the reaction vessel by dissolving the material in pentane and subsequently transferring the resulting solution to an NMR tube for the purpose of identification. Using small amounts of pentane as the solvent for the diiodocarborene assisted in the removal of AlCl_3 impurities.

Iodination of $\text{C}_2\text{B}_5\text{H}_7$ with I_2 in the Absence of a Lewis Acid Catalyst. Molecular iodine (0.5 mmol), dissolved in ca. 0.3 mL of pentane, was added to a glass bulb fitted with an NMR tube. After $\text{C}_2\text{B}_5\text{H}_7$ (0.5 mmol) was added to the mixture, the glass bulb was sealed and heated at 252 °C for 24.5 h; subsequent ^{11}B NMR analysis showed that the only boron compounds now present were 3-I-2,4- $\text{C}_2\text{B}_5\text{H}_6$ (25%) and unreacted $\text{C}_2\text{B}_5\text{H}_7$ (75%). Another reaction was carried out with $\text{C}_2\text{B}_5\text{H}_7$ (1.0 mmol), I_2 (1.9 mmol), and pentane (ca. 1.5 mL), sealed in a glass tube and heated at 260 °C for 24.5 h. Cold-column fractionation¹⁰ yielded 3-IC₂ B_5H_6 (0.5 mmol), 5-IC₂ B_5H_6 (0.25 mmol, both emerging from the column at -40 °C), and 3,5-I₂ $\text{C}_2\text{B}_5\text{H}_5$ (0.2 mmol) as a low-volatility solid. 3,5-I₂ $\text{C}_2\text{B}_5\text{H}_5$ was dissolved in CCl_4 for both proton and ^{11}B NMR analyses.

The proton NMR chemical shifts and coupling constants for the 3-IC₂ B_5H_6 and 3,5-I₂ $\text{C}_2\text{B}_5\text{H}_5$ species were derived by applying a modified NMRNIT iterative program^{11,12} to simulate the experimentally observed proton NMR data. The results for 3-IC₂ B_5H_6 are as follows: $\delta = 0.25$ for H(1,7); 6.16 for H(2,4); 4.45 for H(5,6), $J[\text{H}(1)\text{H}(5)]$ (and the three symmetry related pairs, $J[\text{H}(1)\text{H}(6)]$, $J[\text{H}(5)\text{H}(7)]$, and $J[\text{H}(6)\text{H}(7)]$)

Table III. Kinetic Data for the Rearrangement of 5,6-Br₂-*closo*-2,4- $\text{C}_2\text{B}_5\text{H}_5$ at 295 °C

total heating time, h	% B,B'-Br ₂ -2,4- $\text{C}_2\text{B}_5\text{H}_5$ isomers ^a				
	5,6-Br ₂	1,5-Br ₂	1,3-Br ₂	3,5-Br ₂	1,7-Br ₂
0	100	0	0	0	0
2.0	32.7	29.5	0.4	37.4	0
3.0	29.7	30.5	0.4	39.4	0
4.0	24.3	30.1	2.1	43.5	0
8.0	24.6	29.7	3.2	42.5	0
24	18.3	27.2	8.0	46.6	0
73	16.2	26.2	18.2	39.3	0
162	13.2	23.2	24.4	39.2	0

^a Average estimated errors in concentration measurements: $\pm 1.5\%$.

Table IV. Kinetic Data for the Rearrangement of 5-I-*closo*-2,4- $\text{C}_2\text{B}_5\text{H}_6$ at 295 °C

total heating time, h	% B-I-2,4- $\text{C}_2\text{B}_5\text{H}_6$ isomers ^a		
	5-IC ₂ B_5H_6	1-IC ₂ B_5H_6	3-IC ₂ B_5H_6
0	100	0	0
22	85.6	9.4	5.1
67	82.8	10.2	6.9
207	65.6	14.6	19.8
422	61.6	15.2	23.2
1093	58.3	16.8	24.9
1693	59.4	14.0	26.6

^a Average estimated errors in concentration measurements: $\pm 1\%$.

Table V. Kinetic Data for the Rearrangement of 5,6-I₂-*closo*-2,4- $\text{C}_2\text{B}_5\text{H}_5$ at 295 °C

total heating time, h	% B,B'-I ₂ -2,4- $\text{C}_2\text{B}_5\text{H}_5$ isomers ^a				
	5,6-I ₂	1,5-I ₂	1,3-I ₂	3,5-I ₂	1,7-I ₂
0	100	0	0	0	0
0.5	94.4	5.6	0	0	0
6.5	28.0	32.5	2.8	36.7	0
11	27.1	26.3	3.3	42.2	1.1
30	28.5	27.2	4.7	38.7	1.0
78	22.5	27.9	10.5	36.7	2.4
126	25.4	24.7	11.6	35.0	3.3

^a Average estimated errors in concentration measurements: $\pm 1.5\%$.

= 0.7 Hz, $J[\text{H}(2)\text{H}(4)] = 4.5$ Hz, $J[\text{H}(2)\text{H}(5)]$, $J[\text{H}(4)\text{H}(6)] = 1.8$ Hz, $J[\text{H}(2)\text{H}(6)] = J[\text{H}(4)\text{H}(5)] = 8.9$ Hz, $J[\text{H}(5)\text{H}(6)] = \text{ca. } 3.9$ Hz. The results for 3,5-I₂ $\text{C}_2\text{B}_5\text{H}_5$ are as follows: $\delta = 4.71$ for H(2,4); 3.35 ppm

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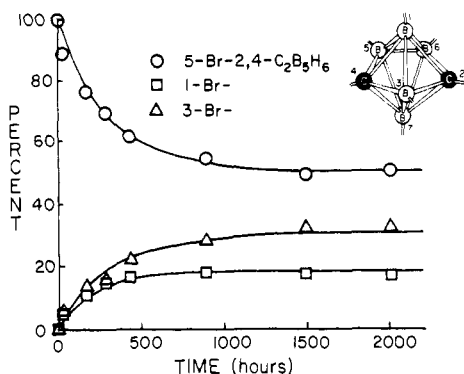


Figure 1. Data (O, □, Δ) for the 295 °C rearrangement of 5-Br-2,4- $C_2B_5H_6$. Curves are fitted to data (Table II) by assuming a DSD mechanism, eq 1, discussed in text. Derived rate constants (h^{-1}): $k_a = 0.0017$, $k_b = 0.0047$, $k_c = 0.21$, $k_d = 0.13$.

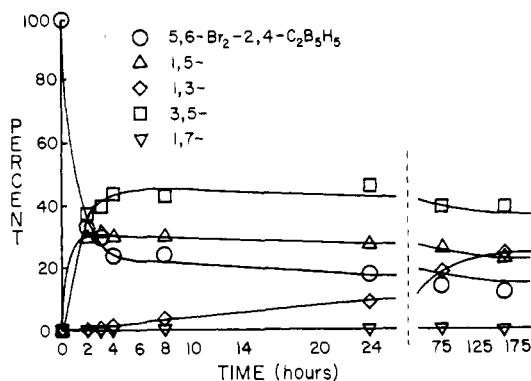


Figure 2. Data (O, Δ, ◇, □, ▽) for the 295 °C rearrangement of 5,6- Br_2 -2,4- $C_2B_5H_5$. Curves are fitted to data (Table III) by assuming a DSD mechanism, eq 2, discussed in text. Derived rate constants (h^{-1}): $k_a = 0.57$, $k_b = 0.82$, $k_c = 0.012$, $k_d = 0.014$, $k_e = 1.46$, $k_f = 0.94$, $k_g = 0.37$, $k_h = 9.1 \times 10^{-4}$.

for H(6), $J[H(2)H(4)] = 3.9$ Hz, $J[H(2)H(6)] = 9.01$ Hz, $J[H(4)H(6)] = 2.1$ Hz.

Kinetic Analyses. Best-fit first-order rate constants were calculated for the $B-X$ -2,4- $C_2B_5H_6$ and B,B' - X_2 -2,4- $C_2B_5H_5$ ($X = Br, I$) rearrangements by using the data given in Tables II–V and assuming a DSD mechanism (see Discussion). The rate constants were determined by using a PROPHET (Bolt, Beranek, and Newman, Inc.) computer program (DIFFEQ-FITDIFF) available through the National Institutes of Health. The best-fit rate constants were subsequently used to generate (using the DIFFEQ-INTDIFF program) rate curves (Figures 1–4) for visual comparison to the measured data.

5- $BrC_2B_5H_6$ Rearrangement. A sample of 5- $BrC_2B_5H_6$ (0.10 mmol) and pentane (0.15 mmol), sealed in a 2-mL glass bulb, which was fitted at one end with a 3-mm NMR tube, was heated at 295 °C for a number of time intervals (Table II) up to a total of 84+ days; after each heating period the sample was immediately cooled to room temperature (at ambient temperatures the rearrangement was essentially quenched) and the percentage composition of isomers (Table II) were determined by boron-11 NMR (160.44 MHz; both coupled and proton-decoupled) analyses. The kinetic data is shown graphically in Figure 1.

5,6- Br_2 -2,4- $C_2B_5H_5$ Rearrangement. In a manner similar to that described for the rearrangement of 5- $BrC_2B_5H_6$, a sample containing 5,6- $Br_2C_2B_5H_5$ (ca. 0.075 mmol) and pentane (ca. 0.03 mL) was subjected to a number of heating periods at 295 °C (Table III). After each heating period the reaction was quenched by cooling the sample to room temperature; subsequently a ^{11}B NMR (160.44 MHz) analysis was conducted to determine the percentage of each dibromocarborane isomer present (Table III and Figure 2).

5- $IC_2B_5H_6$ Rearrangement. A quantity of 5- $IC_2B_5H_6$ (0.1 mmol) was combined with pentane (0.1 mmol) and sealed in a 3-mm NMR tube equipped at one end with a 3-mL glass bulb. The sample was heated at 295 °C for various time intervals (Table IV) and analyzed (Figure 3) in a manner described above for the bromocarborane rearrangements.

5,6- $I_2C_2B_5H_5$ Rearrangement. A sample of 5,6- $I_2C_2B_5H_5$ (0.1 mmol) was combined with pentane (0.3 mL) and sealed into a 3-mL NMR tube equipped at one end with a 3-mL glass bulb. The sample was heated at 295 °C for a number of time intervals (Table V); after each heating

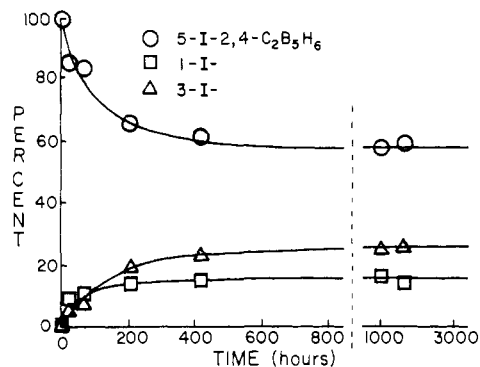


Figure 3. Data (O, □, Δ) for the 295 °C rearrangement of 5- I -2,4- $C_2B_5H_6$. Curves are fitted to data (Table IV) by assuming a DSD mechanism, eq 1, discussed in text. Derived rate constants (h^{-1}): $k_a = 0.0059$, $k_b = 0.023$, $k_c = 0.016$, $k_d = 0.0092$.

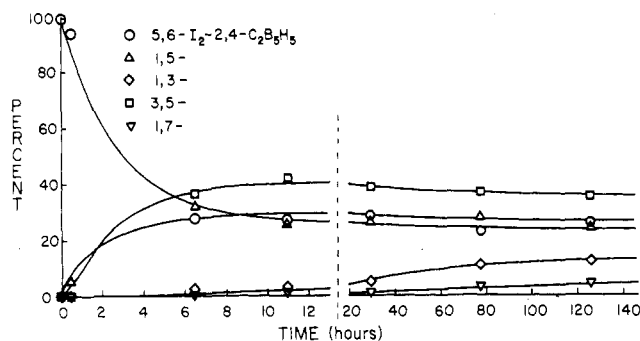


Figure 4. Data (O, Δ, ◇, □, ▽) for the 295 °C rearrangement of 5,6- I_2 -2,4- $C_2B_5H_5$. Curves are fitted to data (Table V) by assuming a DSD mechanism, eq 2, discussed in text. Derived rate constants (h^{-1}): $k_a = 0.25$, $k_b = 0.28$, $k_c = 0.017$, $k_d = 0.0085$, $k_e = 2.07$, $k_f = 1.51$, $k_g = 0.0079$, $k_h = 0.0011$.

period the sample was cooled to room temperature and the percentage composition of each isomer determined by ^{11}B NMR (160.44 MHz) analysis. The results are depicted graphically in Figure 4.

Results and Discussion

In the presence of AlX_3 ($X = \text{halogen}$) all known reactions between molecular halogens and *closo*-2,4- $C_2B_5H_7$ result in the formation of 5-mono- and 5,6-dihalogenated cage products,^{3–6} but the results of similar reactions in the absence of the Lewis acid can be considerably different. We find, in the present study, that iodination of 2,4- $C_2B_5H_7$ in the absence of a Lewis acid catalyst takes place at temperatures in the range of 250–260 °C, resulting in the initial formation of 3- I -2,4- $C_2B_5H_6$ followed by the formation of 3,5- I_2 -2,4- $C_2B_5H_5$. With bromine, however, the bromocarborane product(s) are the same with⁶ or without (present work) AlX_3 . In the case of chlorination, the absence of a Lewis acid catalyst produces a mixture of 1-, 3-, and 5- $ClC_2B_5H_6$; it is to be noted, though, that this reaction was carried out with the encouragement of light.⁴

Brominations of *closo*-2,4- $C_2B_5H_7$ using reactant ratios ranging from 1:2 to 3:1, in the absence of a Lewis acid catalyst and at temperatures up to 200 °C, give rise to the 5- Br -2,4- $C_2B_5H_6$ and 5,6- Br_2 -2,4- $C_2B_5H_5$ species and no other *B*,*B'*-dibrominated carborane isomers. The formation of the 5,6-dibrominated species predominates, of course, when the larger $Br_2/C_2B_5H_7$ reactant ratios are used. The “noncatalyzed” bromination leads to the same products (5- Br and 5,6- Br_2 derivatives of $C_2B_5H_7$) as the presumably Lewis acid catalyzed reaction,⁶ but in lower yields and with more breakdown products (mostly BBr_3); therefore, the catalytic process is the synthetic route of choice for the production of these mono- and dibromocarborane species.

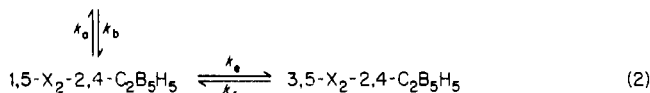
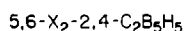
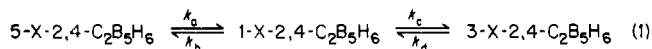
As with the chlorination and bromination^{3,6,13} of $C_2B_5H_7$ using $AlCl_3$ as the catalyst, the $I_2/AlCl_3/C_2B_5H_7$ reaction gives rise to

monoiodination in the 5-position of the carborane. Formation of the 5,6- $I_2C_2B_5H_5$ species is also observed, even when low ratios of $I_2/C_2B_5H_7$ are used, and most probably follows soon after the initial formation of the monoiodo species; thus, the second iodination step is obviously competitive with the first, an indication that the activation energy for a second iodine addition to the cage is similar to that of the monoiodo product formation.

Iodination of $C_2B_5H_7$ with I_2 , in the absence of a Lewis acid such as AlX_3 , takes place at a reasonable rate only when elevated temperatures, ca. 260 °C, are employed; under these conditions the initial monoiodinated product is, as mentioned earlier, 3-I-2,4- $C_2B_5H_6$. Some 5-I-2,4- $C_2B_5H_6$ is frequently produced as well, but is not always present in detectable amounts from every reaction attempt. When the ratio of starting materials, $I_2/C_2B_5H_7$, is raised to nearly 2:1, the diiodo carborane isomer, 3,5- I_2 -2,4- $C_2B_5H_5$, is formed in substantial quantity. These observations are in contrast to the results described above for the $AlCl_3$ -catalyzed reaction of I_2 with $C_2B_5H_7$, which produces the 5-I monosubstituted and 5,6- I_2 disubstituted carborane isomers only. The catalytic nature of the $AlCl_3$ is manifested by the considerably lower temperature, ca. 90 °C, required to effect iodination of the carborane.

The 3-substituted position of $C_2B_5H_7$ has been found to be the thermodynamically favored *B* position with respect to *B*-methyl-^{7,8} and *B*-monochloro-substituted^{3,5} compounds; however, rearrangement results for the *B*-monoiodocarborane (see below) indicates that the 5-iodo isomer is the most stable *B*- $IC_2B_5H_6$. It is thus unlikely that the formation of 3- $IC_2B_5H_6$ from the "uncatalyzed" thermal $I_2/C_2B_5H_7$ reaction is a result of initial 5- or 1-position cage iodination followed by the rearrangement of the product(s), for such a rearrangement should also lead to a measurable quantity of the 1-I-2,4- $C_2B_5H_6$ isomer and/or an amount of 5- $IC_2B_5H_6$ exceeding the yield of the 3-I product. This is not observed. If a radical mechanism for the iodination (sans Friedel-Crafts type catalyst) is involved, it is noteworthy that monoiodo substitution takes place at the 3- and 5-positions only (cf., presumed radical chlorination of $C_2B_5H_7$ gives substitution at all types of cage borons, 1, 3, and 5⁴).

The bromo- and iodocarboranes prepared in the present study all undergo thermal rearrangements at reasonable rates close to 300 °C. The rearrangement patterns for these 5-X and 5,6- X_2 derivatives of 2,4- $C_2B_5H_7$ ($X = Br, I$; Figures 1–4) are reminiscent, with minor digressions, of those observed earlier for 5- $CH_3C_2B_5H_6$,⁷ 5,6- $(CH_3)_2C_2B_5H_5$,⁸ 5- $ClC_2B_5H_6$, and 5,6- $Cl_2C_2B_5H_5$.⁵ And, as with the *B*-methyl and *B*-chloro systems, the rate data gathered at 295 °C for each of the bromo- and iodocarborane rearrangements is consistent with a diamond-square-diamond (DSD) mechanistic scheme in which the two cage carbon atoms are not allowed to move to adjacent, or higher coordination, positions.^{7,8,14–18} This mechanistic premise leads to the schemes in eq 1 and 2, which show the allowable reversible,



pathways between the three *B*-mono- and the five *B,B'*-substituted 2,4- $C_2B_5H_7$ isomers, respectively. A comparison of derived rate constants for the monobromo and monoiodo rearrangements (see

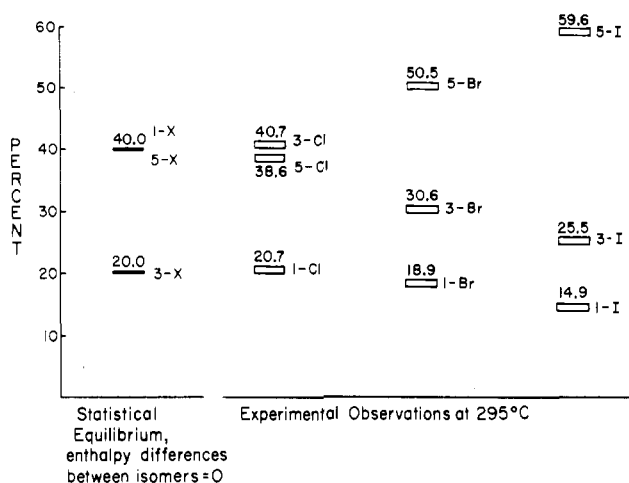


Figure 5. Comparison of observed equilibrium quantities of *B*- X -2,4- $C_2B_5H_6$ isomers ($X = Cl, Br, I$), at 295 °C, with those predicted when no enthalpy differences exist between isomers.

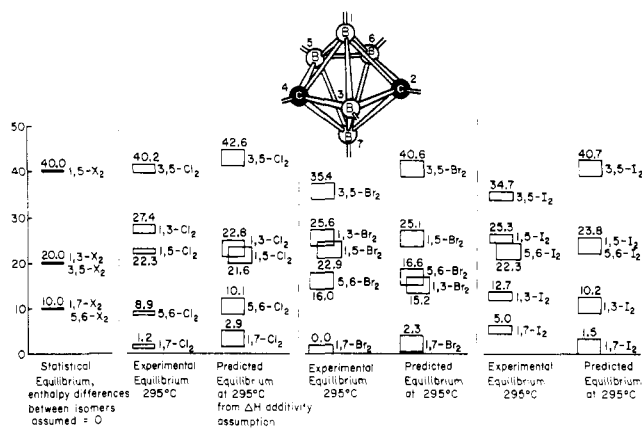


Figure 6. Comparison of observed equilibrium quantities of *B,B'*- X_2 -2,4- $C_2B_5H_5$ isomers ($X = Cl, Br, I$), at 295 °C, with those predicted in which no enthalpy differences exist between isomers.

Figures 1 and 3) indicates that the values for the interconversion of 5- and 1- $BrC_2B_5H_6$ are smaller than those for the corresponding iodo isomer conversion; in contrast, the interconversion of 1- and 3- $BrC_2B_5H_6$ is faster than the analogous 1- and 3- $IC_2B_5H_6$ transformations. Also, it is noted (Figures 2 and 4) that the thermal rearrangements of the corresponding 5,6- $X_2C_2B_5H_5$ compounds to give (eventually) equilibrium amounts of all, or most all, five *B,B'*- $X_2C_2B_5H_5$ ($X = Br, I$) isomers are (at the outset of the rearrangement) significantly faster than the 5- X -2,4- $C_2B_5H_6$ rearrangements.

Other reasonable rearrangement mechanisms to be considered are (a) a triangular-face-rotation (TFR) mechanism^{15,19} in which the two cage carbon atoms are not permitted to move to adjacent, or higher coordination, positions, (b) DSD or TFR mechanistic schemes that allow the separated cage 2,4-carbon atoms of the dicarbaheptaborane to decrease their mutual separation and/or to move to vertices of higher coordination, and (c) a 1,2-substituent (cage-) surface-migration (SSM) mechanism.¹⁹ It is to be noted, however, that the TFR mechanistic scheme defined in category a has been ruled out for the *B*-Me- and *B*-Cl-2,4- $C_2B_5H_6$ thermal rearrangements.^{5,7} Category b type mechanisms appear to be unattractive, in that routes leading to cage species with cage-carbon atoms at either high-coordination axial sites or adjacent cage sites are expected to be energetically unfavorable^{15–18} and thus entail negligible rate constants when compared to similar cage rearrangement processes that can avoid these problems. The SSM mechanism, category c, cannot be ruled out, but seems unlikely based on arguments presented earlier.⁷

(14) Lipscomb, W. N. *Science (Washington, D.C.)* **1966**, *153*, 373–378.
 (15) Miller, W. R.; Grimes, R. N. *J. Am. Chem. Soc.* **1975**, *97*, 4213–4220.
 (16) Dewar, M. J. S.; McKee, M. L. *Inorg. Chem.* **1980**, *19*, 2662–2672.
 (17) Hoffmann, R.; Lipscomb, W. N. *J. Chem. Phys.* **1962**, *36*, 3489–3493.
 (18) Dustin, D. F.; Evans, W. J.; Jones, C. J.; Wiersema, R. J.; Gong, H.; Chan, S.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1974**, *96*, 3085–3090.

(19) Plotkin, J. S.; Sneddon, L. G. *Inorg. Chem.* **1979**, *18*, 2165–2173.

Equilibrium quantities of 5-XC₂B₅H₆ and 5,6-X₂C₂B₅H₅ (X = Br, I) isomers are derived from the best-fit 295 °C "DSD" rate constants and agree, within experimental error, with values obtained from a mechanism-independent graphical inspection method. These equilibrium distributions are displayed in Figure 5 for the monosubstituted carboranes and in Figure 6 for the di-substituted carboranes. The far-left column in each of these two figures represents statistical equilibrium percentages expected for a hypothetical isomer set in which no enthalpy differences exist between isomers. This is based solely on the number of equivalent cage positions a substituent can assume. It is apparent (Figures 1-6) that experimental results vary considerably from the statistical percentages (i.e. no enthalpy differences between isomers), indicating that there is a significant substituent effect on the final isomer equilibria. Also, the degree of departure from these statistical numbers is a measure of the stability, or instability, of any given isomer relative to the other isomers in the set. For comparison to the bromo and iodo systems, the equilibrium values obtained previously for the *B*-chlorocarborane and *B*,*B'*-dichlorocarborane isomer sets⁵ are also displayed in Figures 5 and 6.

If statistical considerations (i.e., the 5- and 6-positions are equivalent, as are the 1- and 7-positions in the parent cage, whereas the 3-position is unique) are *not* taken into account, the relative stabilities of all of the halo derivatives of C₂B₅H₇ shown in Figure 5 follow the positional preference order 5-X > 3-X > 1-X. As the atomic number of the halogen becomes higher, the stability of the 5-X isomer increases, largely at the expense of the 3-X isomer. When statistical contributions to the equilibrium concentrations are factored out, the isomer stabilities follow the order 3-X > 5-X > 1-X for X = Cl and Br and follow the order 5-X > 3-X > 1-X for X = I. Until a molecular orbital approach is found that is satisfactorily sensitive to the energy differences noted here between *B*-X-2,4-C₂B₅H₆ isomers, reasonable explanations for these stability trends will necessarily be rather empirical. Invoking "back-bonding" or "back-donation" of the halogen unshared electrons to the B(3) cage boron may provide a portion of the answer. Chlorine, which can be expected to exhibit a more efficient orbital overlap with boron than can the higher halogens, should back-bond more effectively with the most electropositive boron; and MO studies support that assignment of a high positive boron charge in 2,4-C₂B₅H₇ to B(3).²⁰ Thus, a general increase in 3-X-C₂B₅H₆ stability (relative to the other isomers, 1-X and 5-X, in each set) as the halogen becomes smaller is consistent with this approach. It is more difficult, however, to account for the 5-X stability trend; B(5) is considered the most negatively charged cage atom in the parent compound, a feature that might be expected to favor attachment of the more electronegative, smaller halogens. Because the opposite stability trend is actually observed, perhaps a polarizability argument, which should favor attachment of the larger, more polarizable halogens at the negative B(5) site, might be considered.

After the *B*,*B'*-dibromo and the *B*,*B'*-diiodo isomer groups are allowed to reach equilibrium, the trends in isomer quantities (Figure 6) are similar for four of the five isomers within each set: 3,5-X₂ > 1,5-X₂ > 5,6-X₂ > 1,7-X₂-2,4-C₂B₅H₅. Only the relative amount of the 1,3-X₂ isomer appears grossly different between the systems in which X = Br and in which X = I. When statistically corrected (e.g., "four" compounds, 1,5-, 1,6-, 5,7-, and 6,7-X₂, make up the 1,5-X₂C₂B₅H₅ isomer set, but there is only "one" 5,6-X₂C₂B₅H₅, etc.), the trends in isomer stabilities are 3,5- > 5,6- > 1,3- > 1,5- > 1,7-Br₂-2,4-C₂B₅H₆ vs. 5,6- > 3,5- > 1,5- > 1,3- > 1,7-I₂-2,4-C₂B₅H₆. A comparison of these disubstituted carborane stabilities with the stability trends observed for the corresponding monosubstituted carboranes reveals a degree of consistency: e.g., the monoiodo- and diiododicarbaheptaborane isomers with the iodine(s) attached at the 5- (and/or the sym-

Table VI. ¹¹B NMR Additivity Constants^a for *B*-Halo-2,4-C₂B₅H₆^b Compounds

halogen and position	B(1)	B(3)	B(5)	B(6)	B(7)
1-F	10.31	0.93	1.76	1.76	-21.10
1-Cl	5.63	1.16	-0.49	-0.49	-11.34
1-Br	-0.71	1.17	0.33	0.33	-8.14
1-I	-17.84	1.39	0.74	0.74	-2.80
3-F	3.34	11.15	-2.10	-2.10	3.34
3-Cl	3.37	7.94	-0.59	-0.59	3.37
3-Br	3.67	3.02	0.33	0.33	3.67
3-I	3.58	-11.61	1.47	1.47	3.58
5-F	0.96	-4.28	13.35	-9.85	0.96
5-Cl	1.68	-1.87	9.97	-2.79	1.68
5-Br	1.91	-0.92	4.81	-1.09	1.91
5-I	1.51	-0.07	-11.40	0.42	1.51
6-F	0.96	-4.28	-9.85	13.35	0.96
6-Cl	1.68	-1.87	-2.79	9.97	1.68
6-Br	1.91	-0.92	-1.09	4.81	1.91
6-I	1.51	-0.07	0.42	-11.40	1.51
7-F	-21.10	0.93	-1.76	-1.76	10.31
7-Cl	-11.34	1.16	-0.49	-0.49	5.63
7-Br	-8.14	1.17	0.33	0.33	-0.71
7-I	-2.80	1.39	0.74	0.74	-17.84

^a Based on $\delta(\text{substituted compound}) - \delta(\text{parent compound})$. ^b Values for both *B*-Br and *B*-I isomers are from the present work. Values for *B*-F isomers: (1) Maraschin, N. J.; Lagow, R. J. *Inorg. Chem.* **1975**, *14*, 1855-1859. (2) Ng, B.; Onak, T. *J. Fluorine Chem.* **1985**, *27*, 119-122. For *B*-Cl isomers: Abdou, Z. J.; Soltis, M.; Oh, B.; Siwap, B.; Banuelos, T.; Nam, W.; Onak, T. *Inorg. Chem.*, **1985**, *24*, 2363-2367.

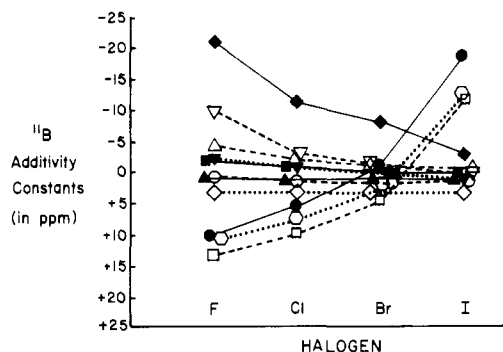


Figure 7. Trends in ¹¹B NMR additivity constants (ppm) for *B*-halogen derivatives of 2,4-C₂B₅H₇; halogen = F, Cl, Br, I. Legend: (◆) 7-position of 1-XC₂B₅H₆; (■) 5,6-positions of 1-XC₂B₅H₆; (●) 1-position of 1-XC₂B₅H₆; (▲) 3-position of 1-XC₂B₅H₆; (○) 1,7-positions of 5-XC₂B₅H₆; (△) 3-position of 5-XC₂B₅H₆; (□) 5-position of 5-XC₂B₅H₆; (▽) 6-position of 5-XC₂B₅H₆; (◇) 1,7-positions of 3-XC₂B₅H₆; (○) 3-position of 3-XC₂B₅H₆; (▽) 5,6-positions of 3-XC₂B₅H₆.

metry-related 6-) positions are generally more stable than the related bromo compounds. If a substituent-positional-preference additivity effect^{5,8} is applied, it is possible to predict equilibrium quantities (Figure 6, columns 5 and 7) of the *B*,*B'*-dihalo compounds from the experimental *B*-monohalocarborane equilibrium results. In this fashion the stability order of all the diiodocarborane isomers is forecasted reasonably well. Within the dibromo isomer set only 1,3-Br₂-2,4-C₂B₅H₅, as noted above, is out of order; the apparently greater stability of the 1,3-Br₂ isomer than that predicted from the additivity effect, is similar to what was found earlier for its dichlorocarborane analogue (see ref 5 and Figure 6, columns 2 and 3).

A ¹¹B NMR chemical shift additivity effect has been previously noted for various *B*-methyl-, chloro-, and nitrogen-substituted *closo*-2,4-dicarbaheptaboranes.^{5,8,21,22} Successful application of this concept to incorporate the bromo- and iodocarboranes prepared in the present study, provides additional evidence for the

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(21) Siwapinyoyos, G.; Onak, T. *Inorg. Chem.* **1982**, *21*, 156-163.

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general usefulness of this type of relationship. From the NMR shifts obtained for the monobromo and monoiodo carboranes (Table I) appropriate additivity constants can be derived by comparing the chemical shifts of each boron position of the substituted carborane with the corresponding position of the parent $C_2B_5H_7$. These additivity parameters, along with those derived from the corresponding fluoro² and chloro⁵ compounds, are given in Table VI and are graphically displayed in Figure 7. The trends seen in this figure can be summarized as follows: (a) a downfield shift is observed for the boron atom directly attached to the halogen, with greater shifts observed for borons with smaller halogens; (b) an upfield shift is noted for the boron atom antipodal (i.e. 7-position) to the substituted 1-position, with greater antipodal-boron upfield shifts found when smaller halogens are attached to B(1); (c) as might be reasonably expected, smaller effects are observed for other borons in the cage. The general utility of the additivity parameters to predict the chemical shifts of the dibromo- and diiodocarboranes in the present work is demonstrated by a comparison of experimental with calculated values in Table I (cf. chemical shifts "out-of-brackets" with chemical shifts "in-brackets", respectively). The differences between the observed and calculated shifts average ca. 0.4 ppm, with a slightly better

correspondence noted for the dibromo isomers than for the diiodo isomers.

Acknowledgment. The authors wish to thank the National Science Foundation (Grant CHE-8315951) and the MBRS (B.N., T.B.) and MARC (F.G.) programs, NIH, for partial support of this study. The PROPHET computer network was made available through an NIH biotechnology resources program DDR contract to the CSULA. Most of the ¹¹B NMR data were obtained with a Bruker WM-500 instrument at the Southern California Regional NMR facility at the California Institute of Technology, funded by NSF Grant CHE-7916324; the assistance of Nancy Swick in obtaining some of the spectra is greatly appreciated.

Registry No. 1-Br-2,4-C₂B₅H₆, 98821-51-3; 3-Br-2,4-C₂B₅H₆, 98821-52-4; 5-Br-2,4-C₂B₅H₆, 27733-74-0; 1,3-Br₂-2,4-C₂B₅H₅, 98821-53-5; 1,5-Br₂-2,4-C₂B₅H₅, 98821-54-6; 3,5-Br₂-2,4-C₂B₅H₅, 98821-55-7; 5,6-Br₂-2,4-C₂B₅H₅, 98821-56-8; 1-I-2,4-C₂B₅H₆, 98821-57-9; 3-I-2,4-C₂B₅H₆, 98821-58-0; 5-I-2,4-C₂B₅H₆, 98838-28-9; 1,3-I₂-2,4-C₂B₅H₅, 98821-59-1; 1,5-I₂-2,4-C₂B₅H₅, 98838-29-0; 3,5-I₂-2,4-C₂B₅H₅, 96343-25-8; 5,6-I₂-2,4-C₂B₅H₅, 98821-60-4; 1-F-2,4-C₂B₅H₆, 55124-16-8; 3-F-2,4-C₂B₅H₆, 55124-15-7; 5-F-2,4-C₂B₅H₆, 55124-17-9; 1-Cl-2,4-C₂B₅H₆, 28347-69-5; 3-Cl-2,4-C₂B₅H₆, 28347-93-5; 5-Cl-2,4-C₂B₅H₆, 28347-92-4; 2,4-C₂B₅H₇, 20693-69-0.

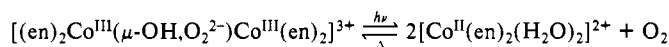
Contribution from the Department of Chemistry, Faculty of Science, Tohoku University, Aoba, Aramaki, Sendai 980, Japan

Photochemical and Thermal Decomposition of $(\Delta\Delta, \Lambda\Lambda)$ - $(\mu$ -Hydroxo) $(\mu$ -peroxo)bis[bis(ethylenediamine)cobalt(III)] Ions in Basic Aqueous Solution

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The title ion in aqueous basic solution does not undergo deoxygenation in the dark, but it does on irradiation with ultraviolet light to give the photoinduced equilibration



The quantum yield determined in the presence of excess EDTA is ca. 2.2×10^{-3} on irradiation at 366 nm at 5 °C and is virtually independent of pH (8.1-10.4). The yield on irradiation at 515 nm at ca. 25 °C is $< 2 \times 10^{-6}$. The ligand(O₂)-to-metal charge-transfer excited state is relevant to the deoxygenation reaction. Continuous irradiation leads to subsequent irreversible decomposition to give cobalt(III) species including $[Co^{III}(en)_2(H_2O)_2]^{3+}$. Such an irreversible decomposition is much slower in the dark (ca. $5 \times 10^{-7} s^{-1}$ at 5 °C, pH 8.9, and $I = 0.1 M (NaClO_4)$; $1 M = 1 mol dm^{-3}$).

Peroxo-bridged and superoxo-bridged dicobalt(III) complexes have been extensively studied to elucidate their chemical and physical properties with reference to the behavior of the coordinated dioxygen moiety.² There are several reports on the photochemical decomposition of $(\mu$ -superoxo)dicobalt(III) complexes³⁻⁶ but none on that of μ -peroxo complexes.⁷ We have recently found that continuous irradiation with ultraviolet light on basic aqueous solutions of μ -peroxo complexes such as

$[(en)_2Co^{III}(\mu-OH, O_2^{2-})Co^{III}(en)_2]^{3+}$ (**1**) (en = ethylenediamine) and $[(dien)(en)Co^{III}(\mu-O_2^{2-})Co^{III}(en)(dien)]^{4+}$ (**2**) (dien = diethylenetriamine) caused reversible redox decomposition to cobalt(II) species and O₂.⁸ Furthermore, both **1** and **2** undergo irreversible decomposition to give mononuclear cobalt(III) complexes on prolonged irradiation.

In the dark, ion **2** undergoes deoxygenation,⁹ while **1** does not.¹⁰ Both **1** and **2** decompose irreversibly and completely to mononuclear cobalt(III) species, after several days at 25 °C.¹¹⁻¹³ The

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