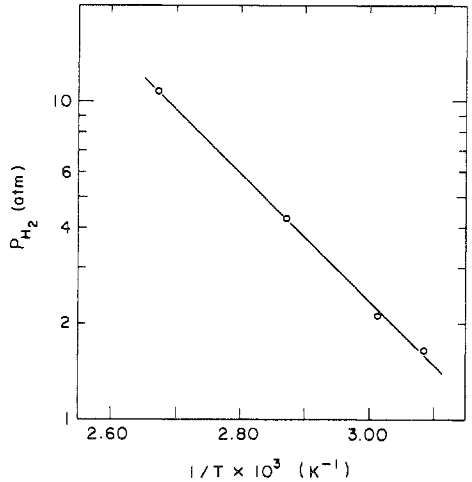

Figure 2. Semilogarithmic plot of P_{H_2} *vs.* reciprocal of the temperature in °K. The pressure plotted is that for the plateau between about $N_H = 2$ and $N_H = 4$ in Figure 1. Since the pressure is not constant in the "plateau region," the midpoint pressure is used.

Table I. Hydrogen Storage, H cm^{-3} × 10^{-22}

Elemental H_2	
Gas (2000 lb/in.^{2}, 300°K)	0.65
Liquid	4.2
Solid	5.2
Metal hydrides	
$LaNi_5H_7$	~8.0
RCo_3H_5 (R = Dy, Ho, Er)	~7.2

$ErCo_3$. Details for the other two compounds will be published later in a full-length article. The equilibrium pressures between the two hydride phases are 3.0, 5.1, and 10.2 atm for $DyCo_3$, $HoCo_3$, and $ErCo_3$ at 100°, respectively. Thus, the trend of hydrogen-escaping tendency which has been observed in the RCo_5 and RNi_5 compounds, *i.e.*, increasing pressure with increasing atomic number of R at one temperature, is also observed in the RCo_3 compounds.

The solubility of hydrogen in RCo_3 was established by exposing these materials to H_2 gas at 40 atm at room temperature. The system produced corresponded to the formula RCo_3H_5.

Kuijpers and Loopstra[6] determined the structure of fully deuterated $PrCo_5$, $PrCo_5D_4$, using neutron diffraction techniques. D was found to reside in portions of the octahedral and tetrahedral interstices; two-thirds of the former and one-third of the latter were filled. Were all of these sites filled, the fully hydrogenated material would correspond to $PrCo_5D_9$. Thus, only four-ninths of the sites are occupied at attainable pressures. In the RCo_3 phases complete hydrogenation, if hydrogen were confined to the tetrahedral and octahedral sites, would give RCo_3H_6. Subject to this assumption the available sites in RCo_3 are five-sixths filled whereas in the RCo_5 phases (if the results for $PrCo_5$ are general) the sites are only four-ninths filled. This higher fractional occupancy supports the initial supposition that the RCo_3 are better hosts for hydrogen than their RCo_5 counterparts.

There is linearity when $\log P_{eq}$ for the $ErCo_3$-H system is plotted against $1/T$ (Figure 2) corresponding to the expression

$$\log P(\text{atm}) = 5.67 - 2013/T$$

The heat of reaction corresponding with the slope in Figure 2 is −9.2 kcal/mol of H_2. This is somewhat more exothermal than the process for the RCo_5 systems, again indicating that RCo_3 is a better host for H_2 than RCo_5.

In Table I the hydrogen storage capability of the RCo_3 compounds is compared with that of $LaNi_5$. Also included are data for hydrogen in solid, liquid, and gaseous forms.

Acknowledgment. This work was assisted by a contract with the U. S. Atomic Energy Commission.

Registry No. $DyCo_3$, 12187-40-5; $HoCo_3$, 12140-00-0; $ErCo_3$, 12134-04-2; H_2, 1333-74-0.

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(6) F. A. Kuijpers and B. O. Loopstra, *J. Phys. (Paris)*, 32, C1 (1971).

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Field Ion Mass Spectra of Boron Hydrides[1,2]

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Received February 12, 1973 AIC40095S

Electron beam ionization of boron hydrides produces many fragments, and the parent ion minus two hydrogen atoms (p − 2) is often the highest mass which will yield a signal of significant intensity. Although parent ions are observable in hydrocarbon electron beam spectra, much fragmentation also occurs. In contrast, field ion spectra of hydrocarbons often consist of a parent ion signal only.[3,4] Consequently it was thought that this technique might be useful for obtaining simplified spectra of boron hydrides containing observable parent ion signals.

It is evident from the data in Tables I and II that parent ion signals of significant intensity can be obtained and fragmentation is clearly diminished. A feature not seen in the electron beam spectra is the presence of species with masses higher than the parent ion. These must result from ion-molecule reactions or proton-capture processes, effects which can readily occur under field ion conditions.[5] When interpreted in terms of ^{11}B, the heaviest mass in the B_4H_{10} spectrum is only p − 1. However, the parent ion at *m/e* 54 was seen sporadically and in the isotopic form $^{11}B_3{}^{10}B$ it would contribute to mass 53. The resolution at which the spectra were obtained (500 ppm) was lower than that necessary to identify monoisotopic signals (<200 ppm).

Calibration of the spectra in Table I was accomplished using acetone or bromobenzene as standards. Of the possible standards in the correct mass ranges, these were found to give the most reproducible signals. Bromobenzene had the added advantage of two isotopic parent ions for comparison. The "peak matching" technique allowed mass determination to the nearest whole mass number or better; the accuracy was dependent upon the degree of attendant "noise." Decrease or complete loss of sample signal intensity was observed for the spectra in Table II during calibration. This may have

(1) Support provided by NSF Grant GP-28928X.

(2) L. A. Larsen, Ph.D. Thesis, University of Washington, 1971.

(3) J. Roboz, "Introduction to Mass Spectrometry Instrumentation and Techniques," Interscience, New York, N. Y., 1968.

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Table I[a]

Compd	Mass	Rel intens
1,1,4,4-Tetramethyl-1,4-diazonia-2,5-diboratocyclohexane[b]	144	6.6
	143	48.7
	142[c]	100.0
	141	44.9
	140	9.2
Tetraborane(10)	53.142[d,e]	100.0[f]
	52.140	57.6
	51.135	64.9
	50	35.1
Pentaborane(9)	65.167[d,g]	11.3
	64.159	100.0
	63.160	84.5
	62.164	56.3
	61.168	7.0
	60.090	11.3

[a] Mass scale calibrated by peak matching. Theoretical parent masses based upon ^{11}B isotope. [b] T.-H. Hseu and L. A. Larsen, paper in preparation. [c] Found by comparison to bromobenzene: 142.099 and 142.080 using both bromine isotopes. Theoretical parent ion mass 142.181. Only this peak was calibrated precisely. [d] Acetone standard. [e] Theoretical parent mass 54.115. [f] Intermittent signals at *m/e* 40, 43, 47, and 54–57. [g] Theoretical parent mass 64.117.

Table II[a]

Compd	Mass	Rel intens
$Me_3NB_3H_7$	115 ± 3[b,c]	21.8
	114	68.3
	113	100.0
	112	98.0
	111	43.6
	110	5.9
	101 ± 1[c]	8.8
	100	37.0
	99[d]	100.0
	98	80.0
	97	54.7
	96	11.2
	73 ± 1[e]	22.4
	72	22.9
Me_3NBH_3	75[f]	3.8
	74	57.0
	73	100.0
	72	24.5
	71	1.4

Compd	Mass	Rel intens
Me_3NBH_2Br	158 ± 6[c,g]	85.2
	157	63.6
	156	100.0
	155	63.6
$(Me_2NPF_2)_2 \cdot B_2H_4$	261 ± 10[c,h]	30.9
	260	90.9
	259	82.0
	258	46.5
	257	9.4
	256	7.0
	255	3.5
	157 ± 6[c,i]	10.0
	156	52.6
	155	32.6
	154	74.4
	153	41.2
	137 ± 4[c,j]	76.5
	136	41.8
	135	39.4
	134	15.3
	127 ± 3[c,k]	100.0
	126	60.0

[a] Mass scale calibrated by substitution; Me = methyl. [b] Product resulting from interaction with acetone; intensities calculated independently of sample. [c] Mass assignments determined from "perfluor" comparison. [d] Theoretical parent mass 99. [e] Likely from Me_3NBH_3. [f] Mass assignment uncertainty by the calculation method ±0; theoretical parent mass 73. [g] Theoretical parent masses 153 and 151 (two Br isotopes). [h] Theoretical parent mass 252. [i] Probably due to $b \cdot B_3H_7$ and/or $b \cdot B_3H_5$ species resulting from reactions in the ion source; theoretical masses 153 and 151. [j] Parent ion minus one base molecule; theoretical mass 139. [k] "Half-molecule;" theoretical mass 126.

resulted from the necessarily reduced source sample pressures or from sample–standard reactions. In the case of $(CH_3)_3N \cdot B_3H_7$ with acetone as a standard this resulted in an unidentified product with a mass heavier than that of the borane adduct.

The "substitution" technique of calibration, used to circumvent signal suppression, had uncertainties in mass assignments which were sometimes quite large. This is unfortunate because it is important to distinguish between parent ions and their proton adducts, often abundant among spectrometer source reaction products. For example, the spectrum of B_5H_9 contained a contribution from the adduct $B_5H_{10}^+$. Chemical ionization yields like results for pentaborane(9), hexaborane(10), and B_2D_6.[6] Of these, only B_6H_{10} becomes protonated in solution.[7] If field ionization is to confirm the similar basicity of other boron compounds and to demonstrate which fragment species are important under these conditions, it will be necessary to use a more accurate means than "substitution" to calibrate the spectra.

The tabulated spectra are the average results of several consecutive spectra for each compound, since signal intensities varied significantly. This variation is not unique to boron compounds; it has also been observed for petroleum fractions under nearly identical mass spectrometer conditions.[8] This is presumably the reason the intensity distributions for B_4H_{10} and B_5H_9 do not correspond well to the statistical scrambling of ^{11}B–^{10}B.

In addition to the compounds listed, diborane(6) was examined, but no consistent spectra could be obtained. Some alkylated diborane(6) derivatives, however, have been shown to have very weak spectra which were successfully calibrated by the "peak matching" techniques using acetone as a standard.[9]

Experimental Section

These spectra were obtained upon an AEI-MS9 high-resolution mass spectrometer,[10] fitted with the manufacturer's combined FI/EB source. Instrument sensitivity was adjusted in the EB mode using perfluorotributylamine ("perfluor"). The FI mode was operated at ambient temperature and at pressures $\leq 5 \times 10^{-5}$ Torr. Spectra were calibrated in either of two ways, by the usual "peak matching" technique, using bromobenzene or acetone as a standard, and by "substitution." Substitution calibrations were accomplished by decreasing

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(6) J. J. Solomon and R. F. Porter, *J. Amer. Chem. Soc.*, 94, 1443 (1972); R. C. Pierce and R. F. Porter, *ibid.*, 95, 3849 (1973).
(7) H. D. Johnson, II, V. T. Brice, G. L. Brubaker, and S. G. Shore, *J. Amer. Chem. Soc.*, 94, 6711 (1972).
(8) W. L. Mead, *Anal. Chem.*, 40, 743 (1968).
(9) L. Cox, unpublished results.
(10) Purchased with funds provided under National Science Foundation Instrument Grant GP-5418.

the magnetic field strength (*i.e.*, "sweeping" the spectrum from the high-mass end to the low-mass end) and admitting acetone into the source after the sample signals had been obtained. The spectrum was then matched to an electron beam generated spectrum of perfluorotributylamine using the acetone signals as indices. In some cases, the mass instead was calculated using mass separation distances for sample peaks and for the p and p + 1 signals of acetone and the distance between voltage markers in the two regions of the spectrum.

Acknowledgment. The authors thank William Howald for assembling the field ion equipment and for aiding in these experiments.

Registry No. 1,1,4,4-Tetramethyl-1,4-diazonia-2,5-diboratocyclohexane, 14102-49-9; tetraborane(10), 18283-93-7; pentaborane(9), 19624-22-7; Me$_3$NB$_3$H$_7$, 12447-20-0; Me$_3$NBH$_3$, 75-22-9; Me$_3$NBH$_2$Br, 5275-42-3; (Me$_2$NPF$_2$)$_2$·B$_2$H$_4$, 32049-77-7; (Me$_2$NCH$_2$-BH$_2$)$_2$, 50830-61-0.

Contribution from the Department of Chemistry,
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Boron-11 Nuclear Magnetic Resonance Shift Assignments for 8-Iodo-1,2-dicarbadodecaborane(12) and Related Compounds

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Received March 12, 1974 AIC40167F

Preliminary ^{11}B chemical shift assignments have been made for 1,2-dicarbadodecaborane(12)[1] (*o*-carborane) and several halogenated derivatives.[2] These assignments have been made primarily on the basis of molecular symmetry and chemical evidence. Because of the characteristic small chemical shift range of carboranes, $J_{\mathrm{B-H}}$ is often of a magnitude comparable to the chemical shifts and proton decoupling has been extensively used to simplify the spectra. The ^{11}B–^{11}B nmr double-resonance technique,[3,4] combined with off-resonance proton decoupling and the dispersion of chemical shifts available at 60 kOe has enabled us to assign all of the ^{11}B chemical shifts for 8-iodo-*o*-carborane.[5]

An *o*-carborane[6] substituted in the 8 position has C_s symmetry, with its one symmetry plane passing through B(3), B(6), B(8), and B(10). The spectrum therefore should consist of three doublets of relative area 1 for B(3), B(6), and B(10) and an area 1 singlet for the substituted B(8) and three doublets of area 2 for the three symmetry-equivalent pairs, B(4), B(7); B(5), B(11); and B(9), B(12).

The 80.2-MHz ^{11}B nmr spectrum of 8-iodo-*o*-carborane (Figure 1) shows resonances attributable to nine boron atoms. A singlet of relative area 1 is evident as the most shielded boron and three doublets of area 2 and two doublets of area 1 are readily discerned. On partial decoupling of the protons, with a concomitant decrease in the doublet spacing, one of the lines splits into two resonances to reveal the hidden doublet at 32.7 ppm.

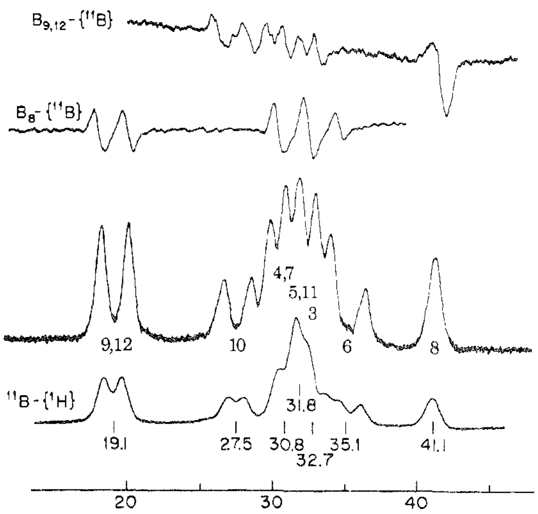

Figure 1. ^{11}B nmr assignments and double-resonance experiments for 8-iodo-*o*-carborane. The bottom scale and chemical shifts are in ppm from trimethyl borate. In the lowest spectrum ^{11}B-{^{1}H} indicates that the ^{11}B spectrum was observed with partial ^{1}H decoupling. The top two traces resulted from the ^{11}B–^{11}B double-resonance experiments. That boron which was observed is denoted as B$_n$.

The singlet at 41.1 ppm relative to trimethyl borate[7] is assigned to B(8). Three ^{11}B–^{11}B double-resonance experiments[3] were performed to identify the remaining resonances. The intensity of the B(8) resonance was monitored as a second radiofrequency field was swept through the rest of the spectrum. The singlet B(8) resonance showed coupling to the two-boron doublet at 19.1 ppm, the two-boron doublet at 30.8 ppm, and the hidden one-boron doublet at 32.7 ppm. We expect B(8) to be coupled to B(9), B(12); B(4), B(7); and B(3); therefore we assign the hidden doublet at 32.7 ppm to B(3). The two-boron doublet at 19.1 ppm must be either B(9), B(12) or B(4), B(7). We found it to be coupled to the two-boron doublet at 30.8 ppm, the two-boron doublet at 31.8 ppm, the one-boron doublet at 27.5 ppm, and the singlet B(8). The resonance at 19.1 ppm cannot be due to B(4), B(7) because the only unique borons which should be coupled to B(4), B(7) are B(8) and B(3), both of which have already been assigned to resonances other than that at 27.5 ppm. Therefore, we assign the resonance at 19.1 ppm to B(9), B(12). The one-boron doublet at 27.5 ppm, to which B(9), B(12) is coupled, we assign to B(10). The remaining one-boron doublet at 35.1 ppm must be assigned to B(6). Of the pair of two-boron doublets which remain to be assigned, the one at 30.8 ppm is assigned to B(4), B(7) because it is coupled to B(8) and the one at 31.8 ppm is assigned to B(5), B(11). To confirm these assignments, a third experiment was performed which showed B(10) to be coupled to B(9), B(12); B(5), B(11); and B(6) as expected.

The shift of B(8) in the title compound (41.1 ppm) is in such strong contrast to the shifts of the iodinated boron atoms in 9,12-diiodo-*o*-carborane (24.0 ppm) and 9,10-diiodo-*m*-carborane (22.4 ppm) reported by Stanko, *et al.*,[2] that we were led to examine their assignments in detail. Our experience with the halodecaborane(14) series,[4] their 6,9-bis(dimethyl sulfide) diligando derivatives,[8] and dihalodecaboranes[9]

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(1) (a) R. L. Pilling, F. N. Tebbe, M. F. Hawthorne, and E. A. Pier, *Proc. Chem. Soc., London*, 402 (1964); (b) J. A. Potenza, W. N. Lipscomb, G. D. Vickers, and H. Schroeder, *J. Amer. Chem. Soc.*, 88, 628 (1966).

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(4) R. F. Sprecher, B. E. Aufderheide, G. W. Luther III, and J. C. Carter, *J. Amer. Chem. Soc.*, 96, 4404 (1974).

(5) 8-Iodo-*o*-carborane was prepared by condensation of 2-iodo-6,9-[S(CH$_3$)$_2$]$_2$B$_{10}$H$_{11}$ with methyl propiolate followed by decarbomethoxylation with potassium *tert*-butoxide.

(6) Detailed drawings and numbering schemes for *o*- and *m*-carboranes can be found in R. N. Grimes, "Carboranes," Academic Press, New York, N. Y., 1970.

(7) Chemical shifts were taken on a 0.1 *M* sample of 8-iodo-*o*-carborane in methylene chloride and referenced by replacement to a 0.1 *M* sample of trimethyl borate in methylene chloride.

(8) B. E. Aufderheide and R. F. Sprecher, unpublished results.