

concentrations $\text{pH} < 4$ under consideration. It is unlikely therefore that for the conditions investigated a nonbridging hydroxo group will be effective in labilizing a hydroxo bridge and certainly not to the exclusion of k_3 and k_4 . The conjugate-base mechanism does not seem to be relevant either in the first hydroxo-bridge cleavage of the dimer $[(\text{H}_2\text{O})_4\text{Fe}(\text{OH})_2\text{Fe}(\text{H}_2\text{O})_4]^{4+}$, $[\text{H}^+] = 0.2\text{--}1.5\text{ M}$, and the hydrogen ion dependence observed is of the form (1).¹¹

The study by DeMaine and Hunt² on I includes data at pH 's 2.2–4.0, and identification of a term k_0 which is independent of $[\text{H}^+]$. No attempt was made to explain this term. According to the mechanism (3)–(6) the behavior could be adequately represented by the first term in (7) with $(k_4 + k_{-1}) \gg k_3[\text{H}^+]$. For this condition k_2 , k_4 , and k_{-1} are the only effective paths. With $[\text{H}^+]$ in the range 0.05–0.50 M , the second term in (7), which is of the form $a[\text{H}^+]/(1 + b[\text{H}^+])$ appears to be dominant. It is possible from the appearance of Figure 2 in the DeMaine and Hunt paper that the third term with an $[\text{H}^+]^2$ dependence in the numerator may be effective over the range $[\text{H}^+] = 0.5$ to 1.0 M . We also note that El-Awady and Hugus¹ in their study of I require an $[\text{H}^+]^2$ dependent term in the rate law. Data obtained by Rasmussen and Bjerrum¹² for acid cleavage of I at $[\text{H}^+] < 0.05\text{ M}$ fit a dependence of the form (1), which is again consistent with (7) providing $(k_4 + k_{-1}) \gg k_3[\text{H}^+]$. Hoffmann and Taube³ have studied the hydroxo bridge cleavage of the complex $(\text{NH}_3)_4\text{-Co}\cdot\mu(\text{OH},\text{OH})\cdot\text{Co}(\text{NH}_3)_4^{4+}$, and for the range of $[\text{H}^+]$ investigated find their data give an adequate fit to a rate law of the form $a[\text{H}^+]/(1 + b[\text{H}^+])$. Also Lee Hin-Fat and Higginson¹³ have reported data for the hydroxo-bridge cleavage of $(\text{C}_2\text{O}_4)_2\text{Co}\cdot\mu(\text{OH},\text{OH})\cdot\text{Co}(\text{C}_2\text{O}_4)_2^{4-}$ at pH 3.5–4.5, and find a first-order $[\text{H}^+]$ dependence.

We wish to make two further points with regard to experimental procedures. Firstly for the reaction of II, a single-bridged 5+ species, it is necessary to adjust the ionic strength with LiClO_4 and not NaClO_4 . Thus data obtained at 25° with NaClO_4 , Figure 1, can be fitted to an $[\text{H}^+]$ dependence as in (11), where the term

$$10^3 k_{\text{obsd}} = 5.95 + 4.32[\text{H}^+] + 0.99[\text{H}^+]^2 \quad (11)$$

in $[\text{H}^+]^2$ has no mechanistic significance. For the reactions of III, a double-bridged 4+ species, it is generally found that LiClO_4 and NaClO_4 are equally acceptable for the adjustment of ionic strength.⁵ El-Awady and Hugus¹ used NaClO_4 to adjust the ionic strength in their studies on I which involve a single-bridged 5+ species. Secondly we wish to question the evidence for single-bridged intermediates as presented in Figure 5 of reference 2. We have obtained similar curves, Figure 2, by mixing acid and water with no complex at all, using Durrum–Gibson stopped-flow apparatus. We are concerned as to whether due allowance has been made for such mixing effects.

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Are There Heptaboranes?

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Five B_7 hydrides have been reported on the basis of mass spectrometric evidence.^{1,2} The highest masses observed correspond to the formulas B_7H_{11} , B_7H_{12} , B_7H_{13} , B_7H_{14} , and B_7H_{15} . Ditter, Spielman, and Williams have shown that at least one of the "heptaboranes," B_7H_{15} , is actually a mixture of ethylpentaborane and one or more compounds containing other elements in addition to boron and hydrogen.¹ Partial mass spectra for the three lower heptaboranes have been published.^{3,4} We have been able to evaluate the evidence for the existence of these three heptaboranes using a computer method which determines the elemental formulas of ions found in low-resolution mass spectra. This technique was first applied to the boranes,⁵ and then to borane derivatives which contain one other element with a pair of isotopes.⁶ Finally, the procedure was generalized to include all the elements and all their isotopes.⁷

The automatic computer technique for determining the formulas of ions is based upon the cluster of isotope intensities due to each formula. This procedure is especially powerful for the boranes because of the significant percentage of the second isotope, ^{10}B (20%). The computer program employs a matrix method which solves for all the formulas simultaneously. A least-squares-fit monoisotopic spectrum, restricted to positive solutions, is calculated. One, several, or all of the formulas present in the experimental spectrum may be handled exactly. A measure of the fit of the set of formulas is generated. This is used to choose between alternate sets of formulas. The limitations and sources of error of the procedure have been explored extensively.^{5–7}

Results

The three published mass spectra fall into two groups. The first contains B_7H_{11} only.⁴ The measure of the fit of the appropriate formulas, the root-mean deviation (rmd), for this compound is 1.0. This is within the range found for other boranes, 0.01–1.8.⁵ The isotopic distribution found in B_7H_{11} therefore corroborates the existence of heptaborane(11).

The second class of spectra contains both the spectrum of B_7H_{12} ,³ and the composite spectrum, B_7H_{11} with B_7H_{13} .⁴ The fragmentation patterns in those two spectra are so similar that we shall treat them as one. The major difference is the lack of a peak at mass 90 in the B_7H_{12} spectrum. The rmd for the composite

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(7) E. McLaughlin and R. W. Rozett, *J. Organometal. Chem.*, in press.

spectrum is 3.1, well outside the range found for the other boranes. Any attempt to subtract out B_7H_{11} increased the rmd of the residue. The rmd of B_7H_{12} was 2.1, also outside the range of the boranes. The rmd's therefore lead us to doubt the existence of heptaborane(12) and heptaborane(13).

An attempt was made to find alternate formulas for the composite spectrum. Three possible formulas were developed: $C_2B_5H_{11}$ (rmd 0.88), $B_4H_{14}O_2$ (rmd 0.002), and AlB_5H_8 (rmd 0.93). The first formula was tried because hydrocarbons and alkylboranes are known contaminants of the raw B_4H_{10} . Although these were deliberately removed by the experimenters, they seemed to be possible impurities. A methylcarborane of this formula is known, but its fragmentation pattern is different.⁸ The oxygen-containing formula was introduced because of the possibility of air and/or water contamination of the reactant. The formula containing a single oxygen atom had a rmd greater than the simple borane. No compounds with this formula have been found in the literature, but $B_4H_{10} \cdot 2H_2O$ may exist. The simplest possible aluminum-containing compound was tried because two aluminum diaphragms were used in these shock tube experiments.⁴ No compound of this formula is known. For several reasons, it is not possible to determine the exact formulas present in the composite spectrum. The spectrum is almost certainly that of two or more compounds, and there are probably more ionic species present than there are experimental measurements to determine them. But the main conclusion stands. The isotope cluster technique supports the existence of heptaborane(11) only.

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Synthesis of Poly(carbon monofluoride) in a Fluorine Plasma

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Recently, there has been a large amount of interest, both academic and industrial in poly(carbon monofluoride) $(CF_x)_n$. This interest has been due primarily to the development of some new synthetic techniques at Rice University¹ and to some degree to a process

(1) R. J. Lagow, R. B. Badachhane, J. L. Wood, and J. L. Margrave, "Some New Synthetic Approaches to Graphite-Fluorine Chemistry," in press.

developed in Japan for preparing a similar fluorinated carbon material of low molecular weight from activated charcoals and carbon black.² The material, obtained from fluorination of graphite is the most thermally stable polymeric fluorocarbon material known. It is indefinitely stable to 600° and stable for short periods of time to 800°.

Carbon monofluoride of a composition $CF_{0.92}$ was first prepared by Ruff, Bretschneider, and Elert in 1934.³ In 1959, Rudorff and Rudorff⁴ reported a preparation of carbon monofluorides of compositions $CF_{0.68}$ to $CF_{0.98}$ which ranged from black to off-white in color.^{4,5} The techniques at Rice University¹ employed both high-temperature and high-pressure syntheses to prepare the first perfluorinated carbon monofluoride which had a stoichiometry of $CF_{1.12}$ and was snow white. These syntheses were adaptable to the production of 40 g quantities of pure white carbon monofluoride and also overcame the disadvantage of poor reproducibility which was characteristic of the previous syntheses.

Recently, excitement about the lubrication properties of solid carbon monofluoride has been generated by lubrication engineers at the Lewis Research Center of the National Aeronautic and Space Administration⁶ and at the U. S. Army Frankfort Arsenal.⁷ These studies have shown that carbon monofluoride as a solid lubricant under extreme conditions such as high or low temperatures, high pressures, or heavy loads is very much superior to graphite or molybdenum disulfide. In addition, workers at the U. S. Army Electronic Command at Ft. Monmouth, N. J.,⁸ and industrial workers in Japan have concurrently demonstrated a high potential for carbon monofluoride for use as a cathode material in high-energy batteries.

A structure which was proposed by Rudorff for carbon monofluoride is shown in Figure 1. This structure has been shown to be approximately correct except for the layer stacking⁹ and the fact that carbon atoms on the edges of each layer are divalent and therefore have both axial and equatorial fluorine. As one may determine by examining the carbon/fluorine ratio of the most highly fluorinated graphite, the $CF_{1.1}$ ratio is a result of these axial and equatorial fluorines and the exact stoichiometry varies with the particle size. Therefore only the snow white carbon monofluorides with carbon/fluorine ratios greater than 1 lack the fluorine site deficiencies characteristic of the earlier preparations.

Carbon monofluoride of lower stoichiometry has been normally prepared by the reaction of elemental fluorine with graphite at temperatures in the range 400–600°. It is interesting to observe that graphite does not begin to react with a fluorine atmosphere until 400°, while all carbon compounds containing double bonds will

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