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Preliminary communication

TRIOXADIBOROLANES FROM THE OXIDATION OF METHYLDIBORANE*

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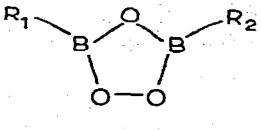
Summary

Mass and IR spectra of unsymmetrical substituted methyltrioxadiborolanes are discussed.

There have been very few studies of the autoxidation of the boranes or their organo derivatives, in the gas phase, in which information upon the nature of intermediates and partial oxidation products has been obtained. The autoxidation of trimethylborane, both in solution [1] and in the gas phase [2] produces the initially formed dimethylboryl(methyl) peroxide which decomposes to dimethoxy(methyl)borane. Another series of intermediates in the oxidation of boranes, the trioxadiborolanes and the boroxines, were identified by Ditter and Shapiro [3] and Lee, Bauer and Wiberley [4], respectively. The first example of a substituted trioxadiborolane was observed as a very minor product in the oxidation of trimethylborane at 125° in the gas phase [5]. This species $(CH_3)_2B_2O_3$ (I, $R_1 = R_2 = CH_3$), a volatile liquid, was recently isolated and fully characterized as a major product in the oxidation of 1,1-dimethyldiborane at ∿80° [6].



(I)

This paper provides the first report of an unsymmetrical trioxadiborolane, 2-methyl-1,3,4-trioxadiborolane, obtained as a product of the reaction between methyldiborane and O_2 at temperatures above 150°C.

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The initial experiments were performed using a mass spectrometric molecular leak system which has been described previously [7]. The next series of experiments involved the use of a specially constructed reaction system whereby gas phase reactions can be carried out; up to 90% of the product mixture introduced into a gas syringe and finally the products injected into a gas chromatograph coupled directly to a mass spectrometer. This system will be described elsewhere.

Two major products in the reaction of $CH_3B_2H_5$ and O_2 are $H(CH_3)B_2O_3$ and $(CH_3)_2B_2O_3$ (i.e. I, $R_1 = H$, $R_2 = CH_3$ and $R_1 = R_2 = CH_3$, respectively) in the mole ratio of $\sim 1/2$. The total yield of these two species is about 25% based on $CH_3B_2H_5$. Other identified products are hydrogen, diborane, hydrocarbons, dimethoxyborane and minor amounts of trimethylboroxine. Well-defined peaks are obtained in the gas chromatogram of the product mixture for both trioxadiborolanes. The mass spectrum of new species $H(CH_3)B_2O_3$ is shown in Fig.1 along with those of $(CH_3)_2B_2O_3$ and $H_2B_2O_3$ for comparison. Noteworthy features in the spectrum of $H(CH_3)B_2O_3$ are the presence of the peaks at 86, 85, 71, 58 and 55 and the absence of a peak at *m/e* 72 (see figure caption for assignments).

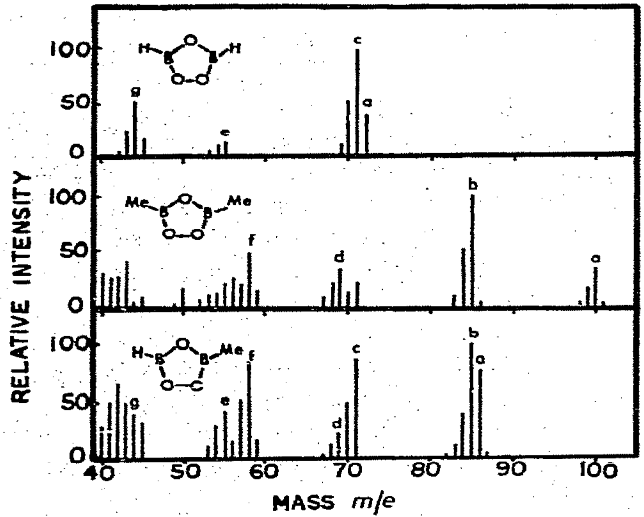

Fig.1. Mass spectra of trioxadiborolanes (run on an AEI MS 1201 B spectrometer at 70 eV). Spectral assignments: a, parent ion; b, $CH_3B_2O_3^+$, c, $HB_2O_3^+$, d, $CH_3B_2O_2^+$, e, $HB_2O_2^+$, f, $CH_3BO_2^+$, g, HBO_2^+.

Experiments performed in an infrared cell provide further information about the unsymmetrical trioxadiborolane*. The spectrum of the product mixture is complex since the spectrum of the dimethyl species overlaps with that of $H(CH_3)B_2O_3$. Thus the broad ring stretching vibrations at 1355 and 1268 cm^{-1} in $(CH_3)_2B_2O_3$ would significantly swamp those bands in $H(CH_3)B_2O_3$. However, the presence of a single band at 2628 and a grouping in the 900 cm^{-1} region is important. The B—CH_3 out of plane bending mode

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*IR spectra were run on a Perkin—Elmer 337 grating spectrophotometer.

expected between 910 and 920 cm^{-1} is also swamped but some sharp bands with fine structure, the most intense being at 883 cm^{-1}, cannot be accounted for in terms of any species other than $H(CH_3)B_2O_3$. Thus tentative assignments are that the 2628 cm^{-1} band is the B—H stretching vibration and the 883 cm^{-1} band, the out of plane B—H bend. A mass spectrum of the contents of the cell ruled out the presence of $H_3B_3O_3$ and $H_2B_2O_3$, both species which would give rise to infrared bands in these regions.

Our studies indicate that $H(CH_3)B_2O_3$ is less stable than both its known analogs. The mass spectral studies indicate that any peroxide precursor to $H(CH_3)B_2O_3$ is too short-lived to be detected by our current techniques. We are now studying this process by a flow technique and will report results of these studies along with those concerned with the isolation of pure $H(CH_3)B_2O_3$ shortly in the complete description of this work.

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