Oxidation of Trimethylborane: Mass Spectral Evidence for the Intermediate $(CH_3)_2B_2O_3$

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Summary The reaction between trimethylborane and oxygen in the gas phase at 125° produces small amounts of the intermediate cyclic $(CH_3)_2B_2O_3$.

CYCLIC $H_2B_2O_3$(I) is the final product in a slow non-explosive reaction of B_5H_9 and O_2 in the gas phase.[1] This reaction was later shown to occur *via* the intermediate boroxine, $H_3B_3O_3$ (II).[2] The same species has been observed as the initial product in reactions of oxygen with B_4H_{10}, BH_3CO, and BH_3PF_3.[3] The cyclic C_{2v} structure has been confirmed

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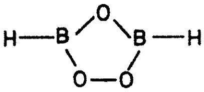
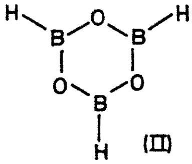
by microwave studies[4] and i.r. spectroscopy.[5] We report evidence for the formation of the hitherto unknown dimethyl derivative, tentatively named 3,5-dimethyl-1,2,4-trioxa-3,5-diborolan.


(I)


(II)

A re-investigation of the gas-phase reaction between $B(CH_3)_3$ and O_2 has been performed, using a mass-spectrometric molecular-leak continuous sampling technique. At ambient temperature the observed initial products are dimethylborylmethyl peroxide, trimethylboroxine, and smaller amounts of higher-molecular-weight species. However, when the reaction is carried out at 125°, new features are observed in the mass spectrum other than those which derive from thermal decomposition of the ambient-temperature products.[6] Groupings appear at *m/e* 100, 99, 98 and *m/e* 85, 84, 83 with relative intensities 22·5, 13·5, 4·5 and 100, 52, 8·8, respectively, indicative of a B_2 species. The only reasonable assignments for the two groupings is that they represent the ions $(CH_3)_2B_2O_3^+$ and $CH_3B_2O_3^+$. Such ions cannot be produced from the fragmentation of higher-molecular-weight cyclic species such as boroxines or alkoxyboroxines. The fragmentation patterns of the latter do not lead to the above type of ions. A correlation between the ion abundance ratios of M^+ and $(M - X)^+$ for the species $X_3B_3O_3$ and $X_2B_2O_3$ ($X = CH_3$ or H) is shown in the Table, together with the predicted values for $(CH_3)_2B_2O_3$ based on the relationship

$$\frac{R[(CH_3)_3B_3O_3]}{R(H_3B_3O_3)} = \frac{R[(CH_3)_2B_2O_3]}{R(H_2B_2O_2)}$$

where $R = 100[I(M - X)^+/I(M^+)]$, I = intensity, and M the parent ion.

Monoisotopic mass spectra for the hydrogenated species were used; these are easily calculated from the normal spectra which are available in the literature.[7] The correlation is seen to be reasonably good.

Attempts to isolate the intermediate from the gaseous product mixtures by low-temperature fractionation and g.l.c. were unsuccessful. I.r. spectra in the gas phase were taken using compensation techniques. The cell in the reference beam contained the decomposition products of the ambient-temperature reaction between $B(CH_3)_3$ and O_2.[6] The decomposition of dimethylborylmethyl peroxide yields essentially the same products at 25° and 125°. The bands observed below 1400 cm^{-1} were at 1360, 1260, 1167, 1118, 928, and 590 cm^{-1}. Tentative assignments based on correlations with the shifts in bands in going from $(CH_3)_3B_3O_3$ to $H_3B_3O_3$ and the spectrum of $H_2B_2O_3$ are that the 1360 and 1167 bands are the inplane ring stretching vibrations, 928 the assymmetrical $B-CH_3$ stretching frequency, and 590 the out-of-plane $B-CH_3$ bending frequency.

TABLE

Compound	I (M^+)	I $(M-X)^+$
$H_3B_3O_3$	21·00	100·0
$(CH_3)_3B_3O_3$ ..	12·45	100·00
$H_2B_2O_3$	41·2	100·00
$(CH_3)_2B_2O_3$ ..	22·5 (observed)	100·00
	24·4 (calculated)	100·00

Experiments based on knowledge of the analogous $H_2B_2O_3$ species were carried out in order to obtain information concerning the mechanism of formation of $(CH_3)_2B_2O_3$. Isolation of $(CH_3)_2BOOCH_3$ and subsequent heating to 125° did not yield $(CH_3)_2B_2O_3$, nor did the reaction of O_2 with pure $(CH_3)_3B_3O_3$ at 125°, prepared in a separate experiment; there was no reaction in this case. Thus the reaction apparently does not proceed *via* mechanisms analogous to that suggested for the production of $H_2B_2O_3$ in the reaction between BH_3CO and O_2[2] nor that suggested for the production of $H_2B_2O_3$ in the reaction between $B_3O_3H_3$ and O_2.[7] One possible mechanism is that $(CH_3)_2B_2O_3$ is derived from partial pyrolysis of the initially formed adduct $B(CH_3)_3 \cdots O_2$,[8] at the higher temperature prior to the rearrangement of the latter to the peroxide.

The electron-impact fragmentation of $(CH_3)_2B_2O_3$ gives rise to a relatively stable cyclic borenium ion $CH_3B_2O_3^+$. It has been pointed out recently that these are rare and are normally expected to be linear.[9] Apparently, $H_2B_2O_3$ and its homologue $(CH_3)_2B_2O_3$, similar to the boroxines, both being six electron systems are stabilised by partial aromatic character. This has been suggested by Coulson for $H_2B_2O_3$[10] and by Armstrong and Perkins for boroxines.[11]

We cannot rule out completely the possible importance of linear polymers in this system. These have been suggested in low-temperature studies[12] and could possibly lead to the ions suggested above. Low-intensity groups of peaks are observed in the mass spectrum at *m/e* 174, 158, and 142. However, their intensity ratios do not correlate with those of the ions at *m/e* 100 and 85 in different runs. Nevertheless, owing to their stability, the ions $(CH_3)_2B_2O_3^+$ could be formed by rearrangements of linear polymers in the ion source of the mass spectrometer, although this is unlikely.

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