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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 $(CH_3)_2B_2O_3$.

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

 $C_{YCLIC} H_2 B_2 O_3(I)$ is the final product in a slow non-explosive and

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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 B₂ 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 highermolecular-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 = CH₃ 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 (CH₃)₃- B_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-CH₃ stretching frequency, and 590 the out-of-plane B-CH₃ bending frequency.

TABLE			
Compound		I (M+)	$I (M - X)^+$
$H_{3}B_{3}O_{3} \dots$ $(CH_{3})_{3}B_{3}O_{3}$ $H_{2}B_{2}O_{3} \dots$ $(CH_{4})_{3}B_{3}O_{4}$	 	21.00 12.45 41.2 22.5 (observed)	100·0 100·00 100·00 100·00
(03/22-3	••	$24 \cdot 4$ (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 (CH₃)₂BOOCH₃ and subsequent heating to 125° did not yield $(CH_3)_2B_2O_3$, nor did the reaction of O_2 with pure (CH₃)₃B₃O₃ 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 H₂B₂O₃ in the reaction between BH₃CO and O₂² 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 (CH₃)₂B₂O₃ gives rise to a relatively stable cyclic borenium ion CH₃B₂O₃+. 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 studies¹² 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 (CH₃)₂B₂O₃+ could be formed by rearrangements of linear polymers in the ion source of the mass spectrometer, although this is unlikely.

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