Pyrolysis of Trimethylborane. Part 2.† Formation of Carbaboranes and other Boron-containing Compounds

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The pyrolysis of BMe_3 has been studied by gas chromatography and mass spectrometry; effects of varying the pyrolysis time and temperature have been investigated. Compounds formed include BMe_2Et, $Me_2BCH_2BMe_2$, carbaboranes $Me_3B_3C_2H_2$, $Me_5B_5C_2H_2$, and 2,4,6,8,9,10-hexamethyl-2,4,6,8,9,10-hexabora-adamantane ($Me_6B_6C_4H_4$). The pyrolysis of BMe_3–H_2 mixtures, in marked contrast to that of pure BMe_3, gives a mixture of carbaboranes of formulae $Me_xH_{(5-x)}B_5C_2H_2$ (x = 2—5) in high overall yield (60—66%). Pyrolyses of BMe_3 in the presence of D_2, C_2H_6, and $HgMe_2$ provide evidence for the involvement of methyl radicals in the reaction.

PREVIOUSLY[1a,b] we have described the formation of several boron-containing compounds, including carbaboranes, from the pyrolysis of trimethylborane. One of these compounds, 2,4,6,8,9,10-hexamethyl-2,4,6,8,9,10-hexabora-adamantane, $Me_6B_6C_4H_4$, the major product

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† Part 1 is ref. 1(*c*)

[1] M. P. Brown, A. K. Holliday, and G. M. Way, (*a*) *J.C.S. Chem. Comm.*, 1972, 850; (*b*) *ibid.*, 1973, 532; (*c*) *J.C.S. Dalton*, 1975, 148.

of the pyrolysis over a wide range of conditions, has been reported on more fully.[1c] In this paper, further studies of the pyrolysis, mainly by gas chromatography and mass spectrometry, are reported, as also is co-pyrolysis with H_2, the presence of which greatly affects the nature of the reaction products. Co-pyrolyses in the presence of D_2, C_2H_6, and $HgMe_2$ are also investigated to provide evidence for the presence of methyl radicals in the decomposition.

RESULTS AND DISCUSSION

Pyrolysis of Pure BMe_3.—Small samples of BMe_3 (0.1 mmol) on pyrolysis in sealed glass phials (0.1 cm^3) gave chromatographs such as those shown in Figure 1.

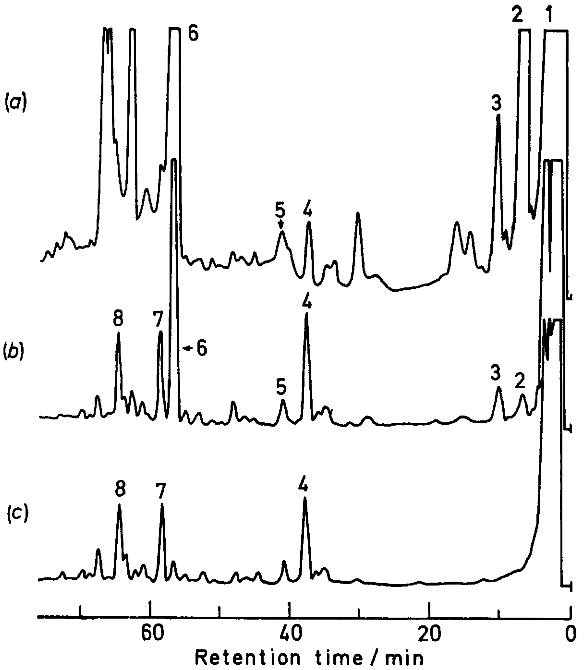

FIGURE 1 Separation of products from heating BMe_3 at 450 °C for (*a*) 20, (*b*) 60, and (*c*) 180 min. The column temperature was programmed at 35 °C for 2 min and then increased by 3° min^{-1} to 200 °C. See Table 1 for identification of peaks

Pyrolyses at 450 °C for 60 min gave fairly good yields of products which in general could be well separated in the chromatography column [chromatograph (*b*), Figure 1]. The major products under these conditions are given in Table 1.

Of most interest is the formation of polyboron compounds and these include $Me_5B_5C_2H_2$ and a compound of probable formula $Me_4EtB_5C_2H_2$ as well as the three compounds $Me_2BCH_2BMe_2$, $Me_3B_3C_2H_2$, and $Me_6B_6C_4H_4$ reported previously. In fact, apart from the volatile components of peak 1 in the chromatograph, the products were almost exclusively polyboron compounds as was easily observed from the complex isotope patterns of the mass spectra, although small amounts of C_6H_6, C_6H_5Me, and C_6H_5Et were detected. The presence of H_2 was not observed, in contrast to reports of previous workers. The most volatile components (peak 1 in the chromatograph) consisted of CH_4 (in large quantities), C_2H_6, unchanged BMe_3, and $SiMe_4$, the last presumably resulting from reaction with the glass vessel, together with BMe_2Et. The presence of several other polyboron compounds was indicated mass spectroscopically but it was impossible even to assign formulae to them. In particular, two very stable compounds corresponding to peaks 7 and 8 and containing 6—8 boron atoms were formed in yields similar to that of $Me_5B_5C_2H_2$ but their mass spectra were complex and contained peaks due to impurities, probably because of mixing with other components in the interface between the mass spectrometer and gas chromatograph.

TABLE 1

Major products of the pyrolysis at 450 °C (60 min)

Peak no.[a]	Compound
1[b]	CH_4, C_2H_6, BMe_3, $SiMe_4$, BMe_2Et
2	$Me_2BCH_2BMe_2$[c]
3	$Me_3B_3C_2H_2$ [2,3,4-Trimethyl-1,5-dicarba-*closo*-pentaborane(5)][c]
4	$Me_5B_5C_2H_2$ [1,3,5,6,7-Pentamethyl-2,4-dicarba-*closo*-heptaborane(7)][d]
5	$Me_4EtB_5C_2H_2$[e]
6	$Me_6B_6C_4H_4$ [2,4,6,8,9,10-Hexamethyl-2,4,6,8,9,10-hexabora-adamantane][f]
7	Unknown compound (*M* 208)
8	Unknown compound (*M* 220)

[a] As shown in Figure 1. [b] Although shown as one peak in Figure 1, these components were separated under conditions more suitable for highly volatile compounds and were identified from their mass spectra. [c] Mass spectrum is identical to samples isolated from the larger-scale experiments.[1c] [d] Mass spectrum is in good agreement with that reported by Seklemian and Williams [4] (see also Table 7). [e] Probable formula; probably a *B*-peralkyl derivative of 2,4-dicarba-*closo*-heptaborane(7). Mass spectrum shows M^+, $[M - 15]^+$, and $[M - 29]^+$ groups of peaks. [f] Mass spectrum identical to authentic sample.[1c]

Yields of these products could not be determined by chromatography due to the impracticability in most cases of calibrating the instrument with pure samples of the compounds, but a rough idea of yields can be obtained from a series of larger-scale experiments (Table 2). The products from these experiments were worked up by trap-to-trap fractionation. Fractions more volatile than $Me_2BCH_2BMe_2$ (peak 2) and less volatile than $Me_6B_6C_4H_4$ were removed and discarded. The remaining products were essentially quantitatively separated into two fractions. The first fraction was a mixture of compounds corresponding to peaks 2—5 and its composition was checked by gas chromatography. The overall yield of this mixture of lower-molecular-

TABLE 2

Pyrolysis of BMe_3 at 450 °C for 1 h

Charge of BMe_3	Amount of BMe_3 decomposed	Yield of $Me_6B_6C_4H_4$		Yield of products corresponding to peaks 2—5	
mg		mg	%	mg	%*
607	131	23	28	9	7
444	148	31	34	11	7
618	143	23	26	10	7

* Calculated on a weight-for-weight basis.

weight products was *ca.* 7% as calculated on a weight-for-weight basis. The molar yield, which could not be calculated without knowing the relative quantities of the separate components, would be significantly higher than this. The second fraction consisted of pure $Me_6B_6C_4H_4$ and was obtained in yields of 26—34%, slightly higher than those previously obtained.

The effect of time on the pyrolysis at 450 °C is shown qualitatively by comparison of the three chromatographs in Figure 1. After 180 min all the BMe_3 has been consumed and only the most-stable products remain [chromatograph (*c*)]. These consist mainly of $Me_5B_5C_2H_2$ and the two unknown components (peaks 7 and 8). The major product after 60 min, namely $Me_6B_6C_4H_4$, has completely decomposed. In contrast, after only 20 min, a much more complex and less completely separated mixture of products is obtained although none of the new compounds could be identified. However, peaks due to the four compounds shown in Table 3 could usually be observed and their areas, which give a rough idea of relative yields, are given.

TABLE 3

Pyrolysis at 450 °C: yields of products as given by peak areas * (arbitrary units)

Product	Duration of pyrolysis/min							
	2	5	20	30	40	50	60	180
$Me_2BCH_2BMe_2$	1.9	2.9	1.6	1.4	0.31	0.11	0.06	
$Me_3B_3C_2H_2$	0.19	0.55	0.40	0.70	0.19	0.15	0.10	
$Me_5B_5C_2H_2$		0.15	0.16	0.20	0.29	0.27	0.31	0.22
$Me_6B_6C_4H_4$		1.7	1.9	2.1	1.6	1.2	1.0	0.03

* Areas are averages from several runs of the same duration. Reproducibility was generally better than *ca.* ±20%.

In another series of experiments the duration of pyrolysis was fixed at 60 min and the temperature varied from 300 to 500 °C. The only products that could be definitely identified as being present throughout the entire temperature range studied were $Me_2BCH_2BMe_2$ and $Me_3B_3C_2H_2$ and their peak areas are given in Table 4.

TABLE 4

Pyrolysis for 60 min at different temperatures: yields of products as given by peak areas (arbitrary units)

Product	θ_c/°C				
	300	350	400	450	500
$Me_2BCH_2BMe_2$	0.48	1.4	1.1	0.06	0.03
$Me_3B_3C_2H_2$	0.04	0.03	0.21	0.1	0.01

It is noteworthy that relatively large amounts of $Me_2BCH_2BMe_2$ are formed at the lower temperatures. Only small quantities of this product were found after 60 min at 500 °C and the mixture of products then obtained was essentially similar to that found after 180 min at 450 °C.

Pyrolysis of BMe_3–H_2 *Mixtures*.—The addition of H_2 in equimolar amounts to BMe_3 greatly affected the nature of the pyrolysis products. Instead of a complex mixture of many different types of boron-containing compounds as reported above a quite different mixture of products, shown by their mass spectra (see below) to consist almost exclusively of methyl-substituted dicarbaheptaboranes, was obtained. Gas chromatographs of the products of pyrolyses in small glass phials (*ca.* 0.05 mmol of BMe_3 and H_2) contained an intense group of closely spaced and well resolved peaks (Figure 2) due to these compounds. Apart from these and a strong peak due to CH_4 and C_2H_6, only a few other weak peaks (unidentified) could normally be observed. The compound $Me_6B_6C_4H_4$, the main product of the pyrolysis of pure BMe_3, could not be detected.

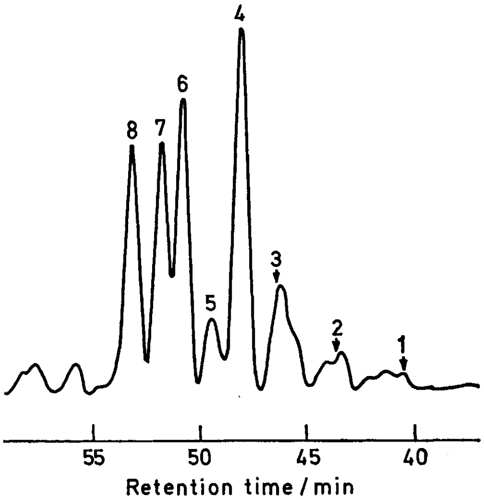

FIGURE 2 Separation of dicarbaheptaborane(7) derivatives obtained by heating a mixture of BMe_3 and H_2 at 450 °C for 1 min. Compounds: $Me_2H_3B_5C_2H_2$ isomers (peaks 1 and 2); $Me_3H_2B_5C_2H_2$ isomers (3 and 4), $Me_4HB_5C_2H_2$ isomers (peaks 5—7); and $Me_5B_5C_2H_2$ (8)

Pyrolysis in the presence of H_2 appeared to be a much ' cleaner ' reaction. The brown air-sensitive polymeric material [2] formed in substantial quantities as a film on the walls of the pyrolysis tubes from the pyrolysis of pure BMe_3 was completely absent although the walls were discoloured brown. Thus the relative simplicity of the chromatographs and the absence of polymeric material suggested a high-yield reaction and this was confirmed by larger-scale experiments, the products of which were worked up by trap-to-trap fractionation. The dicarbaheptaborane mixture was isolated as a fraction containing compounds of closely similar volatility in yields of *ca.* 60—66% (Table 5). These products gave chromatographs consisting solely of a group of peaks similar to that shown in Figure 2.

TABLE 5

Pyrolysis of BMe_3–H_2 (1 : 1) at 450 °C for 15 min

Charge of BMe_3	Yield of dicarbaheptaboranes	Approximate molar yield (%) *
mg		
323	106	65
310	94	60
328	109	66

* Calculated on the assumption that the average composition of the mixture is represented most closely by the formula $Me_4HB_5C_2H_2$.

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[2] J. Goubeau and R. Epple, *Chem. Ber.*, 1957, **90**, 171.

Addition of H_2 also had the effect of increasing the rate of decomposition of BMe_3; for example, when an equimolar mixture of BMe_3 and H_2 was heated at 450 °C there was less BMe_3 remaining after 1 min than there was after 60 min with pure BMe_3. The dicarbaheptaboranes were the almost exclusive products over a very wide range of conditions, although as Table 6 shows the relative amounts of individual compounds varied considerably with reaction conditions.

TABLE 6

Co-pyrolysis of BMe_3 and H_2:[a] yields of dicarbaheptaboranes (chromatographic peak areas in arbitrary units)

Duration of pyrolysis / min	θ_c / °C	Products and isomers[b]							
		$Me_2H_3B_5C_2H_2$		$Me_3H_2B_5C_2H_2$		$Me_4HB_5C_2H_2$			
		I	II	I	II	I	II	II	$Me_5B_5C_2H_2$
60	300			0.4	1.2	0.5	1.3	1.8	4.6
	350		0.2	0.9	1.6	1.1	1.5	2.2	7.1
	400		0.5	1.2	3.7	1.0	3.9	2.8	4.7
	450	1.1	1.8	3.4	6.3	1.0	3.0	2.6	2.4
	500	1.0	1.5	1.8	4.9	1.0	2.6	2.1	1.8
1	400	2.1	1.0	2.3	8.4	1.7	5.1	4.2	3.8
	450	0.7	0.7	3.4	6.5	1.5	5.1	4.2	4.0
	500	0.5	1.1	2.1	5.6	1.5	3.8	3.2	2.4

[a] Mol ratio 1 : 1. [b] In order of increasing retention time.

The mass spectra of these compounds showed the presence of M^+ and $[M - 15]^+$ groups of peaks with isotope patterns indicating the presence of either five or six boron atoms. Because of H loss from these ions, *i.e.* the presence of overlapping peaks due to $[M - 1]^+$ and $[M - 16]^+$ ions, *etc.*, it was not possible to determine the exact number of boron atoms from the relative intensities as directly observed in the multi-isotopic spectra. However, mathematical reduction to monoisotopic form by removal of the ^{10}B and ^{13}C contribution was possible on the assumption of five but not six boron atoms indicating the former as the boron content.[3] This could be done only for those components (Table 7) for which good-quality spectra were obtained. The presence of impurity peaks and poor reproducibility of relative-intensity values for some compounds prevented this from being done in these cases. Loss of H from the M^+ ion took place to a small extent and was of the same order as loss of CH_3. Peaks due to $[M - 29]^+$, which would indicate the presence of ethyl groups, were not observed. It seems highly probable from these spectra and the high stability of the compounds that they are *B*-methyl derivatives of 2,4-dicarba-*closo*-heptaborane(7). This is confirmed by the close agreement between our data for $Me_5B_5C_2H_2$ and those of Seklemian and Williams[4] for the *B*-permethyl derivative of this *closo*-carbaborane. The number of possible $Me_4HB_5C_2H_2$ isomers, assuming a 2,4-dicarba-*closo*-borane structure, is three, the same as that observed. The number of possible $Me_3H_2B_5C_2H_2$ isomers is five, whereas only two were in fact observed.

TABLE 7

Partial mass spectra (reduced to monoisotopic form) of some dicarbaheptaboranes: relative intensities at 70 eV

	Products and isomers[a]					
	$Me_3H_2B_5C_2H_2$[b]		$Me_4HB_5C_2H_2$[c]			
Ion	I	II	I	II	III	$Me_5B_5C_2H_2$[d]
M^+	100[e]	100[f]	100[e]	100[f]	100[f]	100[f]
$[M - 1]^+$	22.6	22.4	16.3	18.2	21.4	16.9
$[M - 2]^+$	11.1	10.4	7.1	10.4	9.7	10.7
$[M - 3]^+$						
$[M - 15]^+$	19.1	28.2	26.5	31.0	29.8	31.5
$[M - 16]^+$	11.7	5.7	4.3	2.3	7.9	7.0
$[M - 17]^+$		8.8		10.9	4.5	

[a] In order of increasing retention time. [b] M 128. [c] M 142. [d] M 156. [e] Residuals <4%. [f] Residuals <2%.

Mechanism of the Decomposition.—The formation of C_2H_6 suggests that $Me^{\bullet}$ radicals are involved. The results of co-pyrolysis experiments with D_2, C_2H_6, and $HgMe_2$, described below, also provide evidence for the involvement of $CH_3^{\bullet}$ radicals.

Thus mixtures of BMe_3 and D_2 (1 : 1) when pyrolysed for 1 h at 450 °C gave MeD and CH_4 in approximately equal amounts. The formation of MeD can be accounted for by equation (1). Mixtures of BMe_3 and C_2H_6 (1 : 2)

$$\mathrm{Me}^{\bullet} + \mathrm{D_2} \longrightarrow \mathrm{MeD} + \mathrm{D} \tag{1}$$

when pyrolysed for 1 h at 450 °C gave an approximately four-fold increase in the yield of BMe_2Et. This can be accounted for by reactions (2) and (3). The latter

$$\mathrm{Me}^{\bullet} + \mathrm{C_2H_6} \longrightarrow \mathrm{CH_4} + \mathrm{Et}^{\bullet} \tag{2}$$

$$\mathrm{Et}^{\bullet} + \mathrm{BMe_3} \longrightarrow \mathrm{BMe_2Et} + \mathrm{Me}^{\bullet} \tag{3}$$

reaction, a homolytic substitution, resembles that of $Me^{\bullet}$ radicals with BEt_3 which is known to occur readily.[5]

In a third set of experiments BMe_3 was heated with $HgMe_2$ as a source of additional $Me^{\bullet}$ radicals.[6] From various experiments at 300 °C increased yields of both BMe_2Et and $Me_2BCH_2BMe_2$ were obtained. These results confirm the importance of $Me^{\bullet}$ radicals in the decomposition.

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[3] M. R. Litzow and T. R. Spalding, 'Mass Spectrometry of Inorganic and Organometallic Compounds,' Elsevier, Amsterdam, 1973, p. 117; J. F. Ditter, F. J. Gerhart, and R. E. Williams, *Adv. Chem. Ser.*, 1968, **72**, 198.

[4] H. V. Seklemian and R. E. Williams, *Inorg. Nuclear Chem. Letters*, 1967, **3**, 289.

[5] J. Grotewold, E. A. Lissi, and J. C. Scaiano, *J. Chem. Soc.* (*B*), 1971, 1187.

[6] S. J. W. Price, 'Comprehensive Chemical Kinetics,' eds. C. H. Bamford and C. F. H. Tipper, Elsevier, London, 1972, vol. 4, p. 217.

EXPERIMENTAL

Chromatographs were run on a Pye 104 instrument using a flame-ionisation detector and helium as carrier gas. The packing was Apiezon L (25%) on Chromosorb P in glass columns 150 cm in length and 0.6 cm in diameter. A Micromass 12 mass spectrometer was interfaced to the gas chromatograph *via* a Watson–Biemann type separator. The BMe_3 was purified by repeated trap-to-trap distillation and stored on the vacuum line.

Sealed-tube Pyrolysis.—Thin-walled phials (0.1 cm^3) made from ' pulled-out ' tubing and having a narrower neck were flamed out *in vacuo*, charged with BMe_3 (0.1 mmol), and sealed at −196 °C using a standard vacuum-line technique. These phials withstood an estimated pressure of 40 atm during pyrolysis with only occasional failures in the electric furnace.* After pyrolysis, about one in three experiments gave irreproducible results, the reason for which was not discovered. In co-pyrolysis experiments, standard techniques were used to measure appropriate quantities of H_2, C_2H_6, and $HgMe_2$. Smaller quantities of BMe_3 were used in these experiments and control experiments with these quantities were carried out.

For large-scale quantitative pyrolyses using BMe_3, tubes 120 cm^3 in volume were used. The reaction tube was connected to the vacuum line, cooled to −196 °C, the seal broken, and the non-condensable gases pumped away. It was then allowed to warm to room temperature and the condensable products were removed, fractionated, and then refractionated on the vacuum line. Ethane was retained at −196 °C, unchanged BMe_3 at −140 °C, the mixture of carbaboranes and $Me_2BCH_2BMe_2$ at −107 °C, and $Me_6B_6C_4H_4$ at −22 °C. The products in the traps at −107 and −22 °C were weighed and subjected to g.l.c. analysis in order to confirm their composition. The yield of $Me_6B_6C_4H_4$ was expressed on a molar basis and the mixtures of carbaboranes and $Me_2BCH_2BMe_2$ were expressed on a weight-for-weight basis (see Table 2). The same procedure was carried out for the mixed pyrolysis of BMe_3–H_2 (1 : 1) and the mixture of dicarbaheptaboranes was retained at −107 °C.

Preliminary Experiments with a Flow System.—An apparatus essentially similar to that described by Goubeau and Epple [2] was used and had a 2-l reservoir, a silica pyrolysis tube (30 × 1.8 cm), U-traps, and a mercury manometer. Initial pressures of BMe_3 were *ca.* 50 cmHg and pyrolysis times were 24—200 h. Circulation of BMe_3 was by thermal convection from the vertical pyrolysis tube which was placed in a furnace at 475—520 °C. Results were poorly reproducible, due in part to sampling problems. The compound $Me_6B_6C_4H_4$ was formed in only very small yield, although from some experiments quantities of $Me_2BCH_2BMe_2$ and $Me_3B_3C_2H_2$ were obtained [1c] as well as smaller amounts of impure $Me_5B_5C_2H_2$. Fractions probably containing the compounds $(MeBCH_2)_x$ ($x = 3$ or 4) (mass spectra showed correct M^+ and $[M - 15]^+$ ions) were also obtained [1c] but the compounds could not be purified.

Reduction of Mass Spectra of Dicarbaheptaborane(7) *to Monoisotopic Form.*—Removal of the ^{10}B contributions from the characteristic M^+ and $[M - 15]^+$ groups of peaks was carried out by the established procedure of successive mathematical subtractions,[3] working from high to low mass within a group of peaks. However, because of the large number of carbon atoms in these compounds, ^{13}C contributions were substantial and had first to be removed. This was done by a somewhat similar process of calculation and subtraction as follows. From the measured intensity of the peak with lowest mass, say m/e n, within a group, the $^{13}C_1$ contribution to the peak at m/e $(n + 1)$ was calculated. This was subtracted from the measured intensity at m/e $(n + 1)$ and from this corrected value at m/e $(n + 1)$ the $^{13}C_1$ contribution to the peak at m/e $(n + 2)$ was calculated and so on throughout the group of peaks. The monoisotopic spectra (Table 7) show the extent to which ions such as $[M - 1]^+$ and $[M - 16]^+$, *etc.*, are present in the M^+ and $[M - 15]^+$ groups of peaks. The measured spectrum over this region for the compound $Me_5B_5C_2H_2$ was as follows (relative intensities in parentheses): m/e 137 (1.6), 138 (8.8), 139 (21.2), 140 (30.5), 141 (23.5), 142 (1.1), 151 (1.6), 152 (6.8), 153 (25.6), 154 (65.0), 155 (100), 156 (76.0), and 157 (4.4).

We thank Dr. C. F. H. Tipper for helpful discussions, and the S.R.C. for awards of a research assistantship (to C. M. W.) and research studentships (to G. M. W. and R. B. W.).

[6/357 *Received, 19th February, 1976*]

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* Throughout this paper: 1 atm = 101 325 Pa; 1 cmHg ≈ 136 × 9.8 Pa; 1 eV ≈ 1.60 × 10^{-19} J.