The Influence of Some Organoboranes on the Gaseous Oxidation of Isobutane

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The rapid and exothermic oxidation of small quantities of trimethylborane initiates the oxidation of isobutane under initial conditions of temperature and pressure where no oxidation normally takes place. Progressive replacement of the methyl groups by methoxy-groups markedly decreases the promoting influence of the additive, although all the organoboron compounds containing B–C bonds are themselves very readily oxidised. An important factor controlling the nature of the organic products derived from the isobutane is the heat evolved during the oxidation of the methylborane and hence the maximum temperature attained in the reacting gas mixture.

THE gaseous oxidation of trialkylboranes is known to yield alkylperoxyboron compounds which are formed by attack of an alkylperoxyl radical on the metal centre[1, 2] [reactions (1) and (2)]. The introduction of reactive metal alkyls into a hydrocarbon–oxygen system has been shown to induce oxidation of the hydrocarbon.

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[1] J. Grotewold, E. A. Lissi, and J. C. Scaiano, *J. Chem. Soc.* (*B*), 1969, 475.

[2] R. C. Petry and F. H. Verkoek, *J. Amer. Chem. Soc.*, 1956, **78**, 6416.

Thus Brokaw *et al.*[3] have shown that triethylborane causes ignition of a n-butane–oxygen mixture within narrow pressure limits at 0 °C. However no analysis

$$R\cdot + O_2 \longrightarrow ROO\cdot \qquad (1)$$

$$ROO\cdot + R_3B \longrightarrow ROOBR_2 + R\cdot \qquad (2)$$

was carried out nor was any explanation given of the involvement of the organoborane in the reaction.

This paper describes the effect of a series of organoboranes on the oxidation of isobutane at initial temperatures well below those where oxidation normally takes place. The boranes used were trimethylborane, methoxydimethylborane, dimethoxymethylborane, and trimethyl borate. Measurements have been made of the pressure and temperature changes accompanying the oxidation and of the amounts of the principal products formed from the hydrocarbon. In the light of the results obtained, suggestions are made as to how the boranes induce oxidation of the hydrocarbon.

RESULTS

(a) *Trimethylborane.*—A mixture containing 5 mole % of the alkylmetal in isobutane was allowed to react with an equivalent quantity of oxygen in the temperature range 100—200 °C. Examples of the characteristic series of temperature and pressure pulses accompanying the reaction are shown in Figure 1. In all the oxidations involving trimethylborane there appear to be three distinct rates of pressure increase although from the plots shown it will be seen that it is not always possible to distinguish the different rates (Figure 1). Furthermore at high temperatures and pressures the reactions are so fast that the pressure is rising rapidly before the admission of the reactants is complete and the reactor has been isolated. The induction periods preceding the reactions are very short (0—0·7 s) and even under mild conditions (100 °C; 70 mmHg pressure) the reaction commences within 0·7 s.

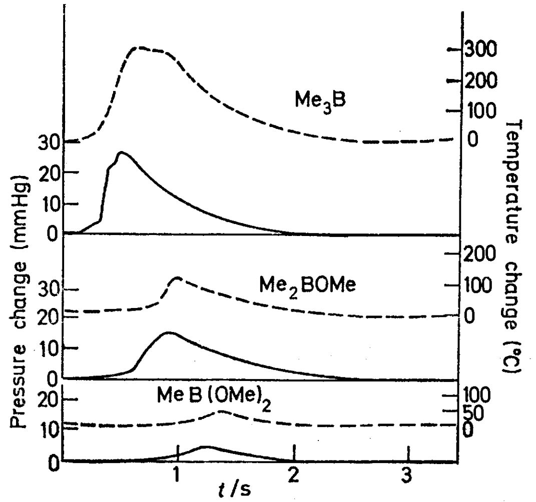

FIGURE 1 Temperature and pressure traces for the oxidation of methylboron compounds in the presence of isobutane. Initial temperature 150 °C; mixture composition $R^1R^2R^3 : Me_3CH : O_2$ 5 : 95 : 100. ——, Pressure change; – – – –, temperature change

These reactions give rise to extremely large temperature increases. Thus with initial temperatures from 100 to 175 °C the maximum temperatures observed rose to *ca.* 600 °C as the initial pressure of reactants was increased to 155 mmHg. Table 1 shows the maximum temperatures associated with the reactants when these are maintained initially at a temperature of 150 °C.

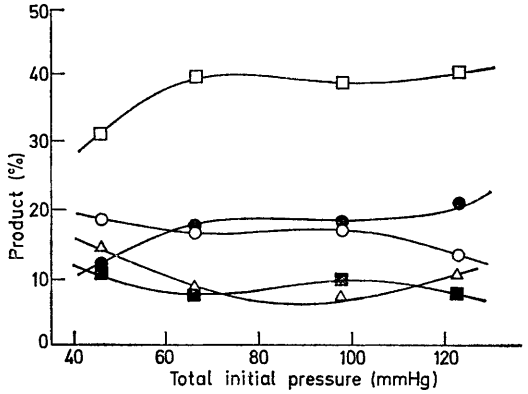

FIGURE 2 The variation of product distribution with initial reactant pressure for the oxidation of trimethylborane in the presence of isobutane. Initial temperature 150 °C; mixture composition $R^1R^2R^3B : Me_3CH : O_2$ = 5 : 95 : 100. □, Isobutene; ■, acetone; ●, propene; ○, acetaldehyde; △, methane

TABLE 1

Temperature increases accompanying the oxidation of isobutane-organoborane mixtures. Initial temperature, 150 °C; $R^1R^2R^3B : Me_3CH : O_2$ = 5 : 95 : 100

Initial pressure (mmHg)	Temperature increase (°C)		
	Me_3B	Me_2BOMe	$MeB(OMe)_2$
20	98	42	5
50	232	93	10
80	341	136	15
110	392	172	20

The influence of pressure on the proportions of the principal products has been investigated for a given reaction mixture (Figure 2). The percentages shown are based on the total products being set equal to 100 and do not reflect the consumption of fuel. It will be seen that isobutene is always the principal product (Figure 2). The minor products, ethane, ethene, propane, isobutyraldehyde, isopropyl alcohol, and t-butyl alcohol, all of which are present in concentrations of <5% have, for the sake of clarity, been omitted. Very similar product distributions were observed throughout the temperature range investigated, although the percentage yield of isobutene increases slightly as the initial temperature is raised. Throughout the temperature range studied the consumption of isobutane also rises from 7 to 11%. The percentage of isobutene formed increases with the associated temperature rise until this reaches 450 °C; above this limiting value, the percentage of alkene in the products remains nearly constant.

The oxidation of the organoborane leads to the formation of trimethyl borate and of a white solid which consists of boric oxide and boric acid.

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[3] R. S. Brokaw, E. J. Badin, and R. N. Pease, *J. Amer. Chem. Soc.*, 1948, **70**, 1921.

Analysis of the organic products formed under fixed reaction conditions (70 mmHg pressure; 100 °C) but after different times (varying from 5 s to 30 min) shows no appreciable change in the product ratio, indicating that all the reaction occurs within the first few seconds. An alteration in the oxygen : isobutane ratio from 0·37 : 1 to 1·38 : 1 also has very little effect either on the product distribution or on isobutene formation.

(b) *Methoxydimethylborane.*—The addition of methoxydimethylborane (5 mol %) to a 0·95 : 1 isobutane–oxygen mixture promotes reaction in the temperature range 125—200 °C. Throughout the range of initial pressures and temperatures studied, the overall pressure and temperature changes and the rates of pressure increase are considerably smaller than in the corresponding studies using trimethylborane (Figure 1 and Table 1). Induction periods are still very short (0—1 s) and decrease as the initial pressure and temperature are increased. Only two different rates of pressure increase can be distinguished (Figure 1) and these would appear to correspond to the first two rates of pressure rise observed with trimethylborane. Analysis shows that the distribution of products is different to that found with the former additive (Table 2).

TABLE 2

Comparison of the products of isobutane oxidation in the presence of different organoboranes. Initial temperature = 150 °C; total initial pressure = 70 mmHg

Product	Product (%) detected in the presence of Me_3B	Me_2BOMe	$MeB(OMe)_2$
Methane	8·42	11·9	0·77
Ethane–ethene	4·70	1·20	
Propane	0·34	0·09	
Propene	17·70	0·04	
Isobutene	40·50	4·71	
Acetaldehyde	16·72	54·24	71·16
Acetone	8·15	23·30	28·07
Isobutyraldehyde	2·94	0·18	
Isopropyl alcohol	0·16	0·34	
t-Butyl alcohol	0·54	2·86	
Isobutane consumed (%)	8·0	3·7	~1

Acetaldehyde is the principal product, together with smaller amounts of methane, acetone, and t-butyl alcohol, and only as the initial reaction temperature approaches 200 °C does isobutene begin to constitute an appreciable proportion of the products. Consumption of the isobutane is only about 3—4% in the presence of this additive.

(c) *Dimethoxymethylborane.*—Replacement of another boron–carbon bond by a boron–oxygen bond further decreases the activity of the organoborane additive. The induction periods are again very short, reflecting the easy oxidation of the remaining boron–carbon bond; pressure increases are very small (amounting to only 1—2% of the initial pressure) and only one rate of pressure rise can be observed (Figure 1). The associated temperature increases are also greatly decreased and Table 1 compares the values obtained for the three boranes studied.

No isobutene was detectable and again acetaldehyde was the most abundant product which was formed together with significant quantities of acetone and methane (Table 2).

(d) *Trimethyl Borate.*—When trimethyl borate was used in the place of the other boranes, no oxidation occurred in the temperature range 150—250 °C.

(e) *Reactions of t-Butyl Hydroperoxide with Trimethylborane.*—The absence of any t-butyl hydroperoxide in these alkylborane-induced oxidations led to a limited number of experiments designed to investigate the fate of any hydroperoxide which might be formed. In mixtures of t-butyl hydroperoxide containing trimethylborane (3·5—7·2 mole %) at an initial temperature of 150 °C all the hydroperoxide was consumed in a thermal ignition, giving the products found to be associated with the oxidation of isobutane together with a few additional species. When the concentration of trimethylborane was kept below 3·3 mole %, the consumption of the hydroperoxide was incomplete but the products were again identical with those of isobutane oxidation. Separate experiments showed that trimethylborate, which was identified as a product of the oxidation of trimethylborane, did not bring about decomposition of t-butyl hydroperoxide at 150 °C.

DISCUSSION

In the absence of an initiator, no oxidation of isobutane occurs in the temperature range 100—200 °C. Di-t-butyl peroxide has been used to initiate the gaseous oxidation of this alkane between 100 and 155 °C and acetone, methanol, t-butyl hydroperoxide, and t-butyl alcohol are the principal products.[4]

The present work shows that methylboranes also induce the oxidation of isobutane at quite low temperatures. Trimethylborane, which is oxidised very rapidly at room temperature to give the peroxyborane, Me_2BOOMe,[2] is the most powerful initiator among the compounds studied and also appears to exert some degree of selectivity. Thus oxidations in the presence of this alkylborane lead to the formation of only ten products (Table 2), whereas at least thirty products are found at higher temperatures in the absence of additives.[5] However the products of reactions involving trimethylborane on the one hand and methoxydimethylborane and dimethylmethoxyborane on the other show a marked contrast (Table 2). In the presence of trimethylborane, >70% of the products are hydrocarbons, principally alkenes, whereas with the other organoboron additives the principal products are carbonyl compounds which, together with other oxygenated species, make up >80% of the total products (Table 2). With all three methylboranes, the product distribution is largely independent of the initial pressure of the reactants and of the isobutane : oxygen ratio; this suggests that the reactions taking place are essentially homogeneous.

The high proportion of alkenes (particularly isobutene) among the products of reactions involving trimethylborane appears to be closely associated with the relatively high temperatures attained (Table 1). Above *ca.* 300 °C, the conjugate alkene is known to be the predominant initial product of the oxidation of

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[4] D. L. Allara, T. Mill, D. G. Hendry, and F. R. Mayo, *Adv. Chem. Series*, 1968, **76**, 40.

[5] G. A. Luckett and R. T. Pollard, *Combustion and Flame*, in the press.

fairly low molecular weight alkanes,[6-8] being formed by the direct abstraction by oxygen of a hydrogen atom from an alkyl radical [reaction (3)].

$$\mathrm{C}_n\mathrm{H}_{2n+1} + \mathrm{O}_2 \longrightarrow \mathrm{C}_n\mathrm{H}_{2n} + \mathrm{HO}_2 \qquad (3)$$

In agreement with this, it has been found that above this temperature the principal product of isobutane oxidation is isobutene.[9,10] In the present work it has been shown that, when trimethylborane is added to isobutane, the maximum temperature attained during the oxidation exceeds 300 °C provided that the initial pressure is greater than 40 mmHg. With methoxydimethylborane, for example, temperatures of this order are reached only at the highest initial pressures used where indeed a small quantity of isobutene is again formed. It is generally agreed that at the relatively low temperatures (<300 °C) which are attained in the presence of the two methoxymethylboranes, fairly small alkyl radicals undergo addition [reaction (4)] rather

$$\mathrm{C}_n\mathrm{H}_{2n+1} + \mathrm{O}_2 \longrightarrow \mathrm{C}_n\mathrm{H}_{2n+1}\mathrm{OO}\cdot \qquad (4)$$

than an abstractive reaction with oxygen. In the case of the t-butyl radical, the resulting t-butylperoxyl radical may perhaps react to give acetone as in reaction (5).[9]

$$\mathrm{Me_3COO}\cdot \longrightarrow \mathrm{Me_2CO} + \mathrm{MeO}\cdot \qquad (5)$$

No generally accepted explanation has been suggested for the formation of acetaldehyde from isobutane, although a mechanism which involves initial oxidative attack at a methyl group has recently been suggested by Luckett and Pollard.[5]

It is perhaps noteworthy that in all the systems in which methylboranes were present no appreciable amounts of t-butyl hydroperoxide could be detected. It might well be expected that this compound would be one of the principal products of the oxidation of isobutane under the relatively mild conditions used.[4] It has been shown in this work that t-butyl hydroperoxide reacts with trimethylborane but not with trimethyl borate. It thus appears likely that, if the hydroperoxide is formed, it can be decomposed specifically by species containing a *boron–carbon* bond and that the interaction of peroxy-species with organoboron compounds may thus partly control product formation in these systems.

In suggesting a more detailed mechanism (for the oxidation of isobutane in the presence, say, of trimethylborane), it must be remembered that the reaction apparently occurs in three distinct stages. The simplest explanation of the three successive pressure pulses (Figure 1) is that an initial bimolecular reaction takes place between trimethylborane and oxygen [reaction (6)].

$$\mathrm{Me_3B} + \mathrm{O_2} \longrightarrow \mathrm{Me_2BOO}\cdot + \mathrm{Me}\cdot \qquad (6)$$

Such a reaction is known to occur in the liquid phase.[11] This reaction produces a sufficient concentration of free radicals to initiate an autocatalytic oxidation involving both isobutane and the organoboron compound. Thus reaction (6) may be followed by reaction (7) and then

$$\mathrm{Me}\cdot + \mathrm{O_2} \longrightarrow \mathrm{MeOO}\cdot \qquad (7)$$

by the two alternative steps (8) and (9). The reactions

$$\mathrm{MeOO}\cdot + \mathrm{Me_3B} \longrightarrow \mathrm{Me_2BOOMe} + \mathrm{Me}\cdot \qquad (8)$$

$$\mathrm{MeOO}\cdot + \mathrm{Me_3CH} \longrightarrow \mathrm{MeOOH} + \mathrm{Me_3C}\cdot \qquad (9)$$

(10)—(16) would then be expected to occur.

$$\mathrm{Me_3C}\cdot + \mathrm{O_2} \longrightarrow \mathrm{Me_3COO}\cdot \qquad (10)$$

$$\mathrm{Me_3COO}\cdot + \mathrm{Me_2CH} \longrightarrow \mathrm{Me_3COOH} + \mathrm{Me_3C}\cdot \qquad (11)$$

$$\mathrm{Me_3COO}\cdot + \mathrm{Me{-}B}\!< \longrightarrow \mathrm{Me_3COOB}\!< + \mathrm{Me}\cdot \qquad (12)$$

$$\mathrm{Me_3COOB}\!< \longrightarrow \mathrm{MeCO}\cdot + \cdot\mathrm{OB}\!< \qquad (13)$$

$$\mathrm{Me_3COOH} + \mathrm{Me{-}B}\!< \longrightarrow\ >\!\mathrm{BOH} + \mathrm{Me}\cdot + \mathrm{Me_3CO}\cdot \qquad (14)$$

$$>\!\mathrm{BO}\cdot + \mathrm{Me_3COOH} \longrightarrow\ >\!\mathrm{BOH} + \mathrm{Me_3COO}\cdot \qquad (15)$$

$$\mathrm{Me{-}B}\!< + \mathrm{Me_3COOB}\!< \longrightarrow\ >\!\mathrm{BOCMe_3} + \mathrm{Me}\cdot + >\!\mathrm{BO}\cdot \qquad (16)$$

The chain-propagating steps involving both the organoborane and the hydrocarbon [equations (10)—(12)] and the various further reactions of the resulting peroxy-species [equations (13)—(16)] presumably manifest themselves as the second rapid pressure increase described earlier (Figure 1). The third oxidation stage (which is identified only for the reaction induced by trimethylborane) clearly involves further reactions of isobutane and hydrocarbon fragments at the rather high temperatures attained to give the observed products; this presumably occurs without the intervention of boron compounds since these have been completely oxidised in the earlier stages and the final oxidation products of the original organoboranes have been shown to have no influence on the oxidation of isobutane. This oxidation of the hydrocarbon on its own at the resulting elevated temperature takes place, however, at an overall rate somewhat lower than that observed in the second stage. The temperature of the reacting gases therefore falls and conditions are eventually attained where no further oxidation can take place.

The most important conclusion drawn from this work is however that the exothermicity of the oxidation of the

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[6] J. H. Knox, *Trans. Faraday Soc.*, 1959, **55**, 1362; 1960, **56**, 1225.

[7] J. H. Knox and C. H. J. Wells, *Trans. Faraday Soc.*, 1963, **59**, 2786, 2801.

[8] R. R. Baker, R. R. Baldwin, and R. W. Walker, Thirteenth International Symposium on Combustion, The Combustion Institute, 1971, p. 291.

[9] A. P. Zeelenberg and A. F. Bickel, *J. Chem. Soc.*, 1961, 4014.

[10] J. Hay, J. H. Knox, and J. M. C. Turner, Tenth International Symposium on Combustion, The Combustion Institute, 1965, p. 331.

[11] M. M. Midland and H. C. Brown, *J. Amer. Chem. Soc.*, 1971, **93**, 1506.

different methylboranes (ΔH^0 for trimethylborane is $-714{\cdot}48 \pm 5{\cdot}36$ kcal mol^{-1} [12]) is one of the principal factors controlling the nature of the oxidation products derived from isobutane. As methyl groups attached to boron are progressively replaced by methoxy-groups, the smaller is the ease of oxidation of the resulting organoboron compound.[13] Thus it appears that the greater the number of boron–carbon bonds present in an alkylborane, the greater will be the exothermicity of its own oxidation and hence also its ability to induce oxidation of a hydrocarbon.

EXPERIMENTAL

Preparation of Organoboron Compounds.—(i) *Trimethylborane*. Methylmagnesium iodide (0·6 mol) in di-n-butyl ether (500 cm^3) was added dropwise with vigorous stirring to boron trifluoride (0·18 mol) in di-n-butyl ether (100 cm^3), under an atmosphere of nitrogen and maintained at 0 °C. Trimethylborane (b.p. −21·8 °C) was passed through pyridine and stored as the solid complex Me_3B,NC_5H_5.

(ii) *Methoxydimethylborane*. Bromodimethylborane was prepared by the method of ref. 14. Tetramethyltin (43·18 g, 0·264 mol) was added dropwise to tribromoborane (66·08 g, 0·264 mol) maintained at 0 °C. The reactants were refluxed for 3 h using a solid CO_2–acetone condenser. The volatile products were distilled off under reduced pressure and the resulting bromodimethylborane (22·7 g, 72%) was redistilled, b.p. 31—32 °C (lit.,[14] b.p. 30—32 °C). Bromodimethylborane (18 g, 0·15 mol) was kept at −196 °C, while methyl orthosilicate (22·84 g, 0·15 mol) was added.[15] The reactants were allowed to warm, and on melting they mixed and their temperature rose to *ca*. 50 °C. Methoxydimethylborane (5·5 g, 50·9%) was then distilled, b.p. 21 °C (lit.,[16] b.p. 21 °C).

(iii) *Dimethoxymethylborane*. The same method was employed as for methoxydimethylborane. Dibromomethylborane (38·74 g, 79·1%), b.p. 62—64 °C (lit.,[14] b.p. 59—62 °C) was prepared from tribromoborane (66·08 g, 0·264 mol) and tetramethyltin (21·59 g, 0·132 mol). The reaction of dibromomethylborane (38·74 g, 0·209 mol) with methyl orthosilicate (31·76 g, 0·209 mol) gave dimethoxymethylborane (12 g, 65·4%), b.p. 53—54 °C (lit.,[17] b.p. 53 °C).

(iv) *Trimethyl borate*. A 40% w/v solution of trimethylborate in methanol–acetone (95 : 5) was purified by the method of Cunningham.[18] Anhydrous lithium chloride was added to the trimethyl borate–methanol azeotrope until two distinct layers were formed. The upper layer was substantially free of methanol, and repeated additions of lithium chloride yielded almost pure trimethyl borate. Fractionation gave pure trimethyl borate, b.p. 69 °C (lit.,[19] 69 °C at 750 mmHg).

Oxidation Technique.—*Preparation of reactant mixtures*. Trimethylborane was liberated from the pyridine complex, under nitrogen, by addition of 25% v/v sulphuric acid to a methanolic solution of the complex. The borane was condensed at −196 °C, degassed, and then admitted to an evacuated storage globe. The other boranes were degassed before storage by the freeze–thaw method. Mixtures were prepared by admitting the boranes to a globe (1 l) at a known pressure and isobutane was then introduced to a pressure such that the mixture contained 5 mole % organoborane.

General oxidation procedure. The isobutane–organoborane mixture was introduced at the required pressure into an evacuated, spherical, Pyrex glass reactor (500 cm^3), enclosed in an electric furnace, *via* an electromagnetic valve. Oxygen was then admitted to give a 1 : 1 fuel–oxygen mixture. Pressure changes were measured by a Bell and Howell (0—25 lb in^{-2}) pressure transducer and temperature changes were monitored by a 0·025 mm diam. platinum–rhodium thermocouple placed at a position where $a/r = 0{\cdot}76$ [20] (where a is the distance from the centre of the vessel and r is the radius). Both measurements were recorded on a Honeywell 1706 Visicorder. Samples for g.l.c. analysis were normally taken 10 s after admission of the oxygen.

G.l.c. analysis. Analysis of oxidation products was carried out on a Perkin-Elmer F11 gas chromatograph using a 8 ft × 0·125 in column of 6·5% w/w bis-2-methoxyethyl adipate and 13·5% w/w di-2-ethylhexyl sebacate on 80—100 mesh Chromosorb P, and a 12 ft × 0·125 in column of 17·5% w/w silicone oil 530 and 2·5% w/w polyethylene glycol on 80—100 mesh Chromosorb W, with temperature programming. (Initial period of 13 min at 30 °C, then linear heating at 30° min^{-1} to 70 °C.)

Analysis of peroxides was carried out on a 4 in × 0·125 in column of 30% w/w dionyl phthalate on 44—60 mesh kieselguhr at 75 °C.[21]

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