144. *Physical and Chemical Properties of Organo-metallic Compounds. Part III. The Oxidation of Boron and Antimony Alkyls.*

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The kinetics of the oxidation of trimethyl- and tri-*n*-propyl-boron have been studied, using the technique described in Part II. The rate is slow enough to be measured only in the case of the trimethyl. This reaction is strongly inhibited by mixtures of boron trifluoride and water. The results are consistent with a chain process, beginning and ending in the walls. Possible reaction schemes are discussed.

The relative rates of oxidation of trimethyl- and triethyl-stibine have been investigated.

The oxidation of the boron and antimony alkyls, like that of the zinc alkyls described in Part II, exhibits the following features: (a) a rapid reaction occurs at pressures well below the ignition limit, and (b) reactions of the methyl derivatives are much slower than those of the higher alkyls. The significance of these points is discussed.

No systematic kinetic studies of the oxidation of the boron alkyls have hitherto been made, although a number of observations on the nature of the oxidation products are on record. Frankland (*J.*, 1862, **15**, 363) stated that slow oxidation of triethylboron produces the diethyl ester of ethaneboronic acid. Krause and Polack (*Ber.*, 1928, **61**, 278) and Krause and Nobbe (*Ber.*, 1930, **63**, 934) studied a number of alkyls, and concluded that the oxidation products were esters of aliphatic boronic acids, or alkylboron oxides. More recently, Johnson and van Campen (*J. Amer. Chem. Soc.*, 1938, **60**, 121) showed that tri-*n*-butylboron is oxidised by dry air to the dialkyl boronate, $BBu(OBu)_2$, exclusively, but with moist air the reaction stops at the half-way stage, BBu_2OBu. They concluded that the " anhydrous autoxidation is a stepwise process, in which the dialkylboronic ester is an intermediate, and that water inhibits further oxidation of the latter." Results described in the present paper are in agreement with the view that the slow oxidation of trimethylboron produces the ester $BMe(OMe)_2$. The reaction is shown to be a chain process, in which chains start and end in the walls, and are mainly without branching except near the ignition limits. As with the zinc alkyls, it appears that the methyl derivative oxidises much less readily than the higher alkyl.

This remark is also true for the antimony alkyls, which have only been studied briefly.

EXPERIMENTAL.

The experimental technique was essentially similar to that described in Part II. As with the zinc alkyls, two series of experiments were carried out : (a) the pressure–time curves were determined for slow admission of one reactant to the other contained in a reaction vessel in a thermostat, and (b) reaction rates at rather higher pressures were measured, the reactants being mixed as rapidly as possible.

Preparation of Materials.—The preparation and purification of the alkyls have been described in Part I. Boron trifluoride was prepared by heating a mixture of potassium fluoroborate and boric oxide (Hellriegel, *Ber.*, 1937, **70**, 689), and condensing the trifluoride in liquid air; after fractionation in a vacuum it was stored in a tube in liquid air. Oxygen and nitrogen were purified as described in Part II.

Results.

(1) *Trimethylboron.*—(a) *Reaction at low pressures.* (i) Determination of Ratio of Reactants. It was found that when the alkyl and oxygen were mixed at pressures which give rise to a slow reaction, the final total pressure was equal to the initial pressure of the reactant present in excess. This is true for all pressures in the range investigated (0·2—10 mm.). The products of reaction appear to be completely gaseous. It follows, therefore, that under the conditions of these experiments, 1 vol. of trimethylboron reacts with 1 vol. of oxygen to give 1 vol. of products.

The products are completely condensable in liquid air. When condensed into a small tube they form a colourless, rather viscous liquid with a characteristic smell. It is fairly stable to air and water and appears to be a single compound. The pressure relations show that it has the formula BMe_3O_2, or probably $BMe(OMe)_2$:

$$BMe_3 + O_2 \longrightarrow BMe_3O_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

(ii) Pressure–Time Curves, and Inhibition of Reaction. Curves (1) and (2), Fig. 1, are *p–t* curves for the slow admission of the alkyl to oxygen, and correspond to initial oxygen pressures of 5·65 and 1·74 mm., respectively. Little measurable

FIG. 1.
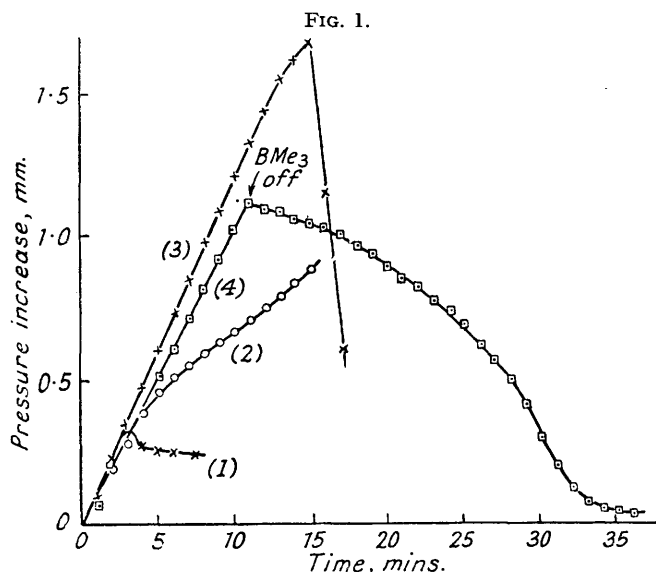
Admission of trimethylboron to oxygen.

Initial pressures :

(1) 5·65 *mm.* O_2.
(2) 1·74 *mm.* O_2.
(3) 5·12 *mm.* O_2 + 0·47 *mm.* BF_3.
(4) 5·97 *mm.* O_2 + 0·43 *mm.* BF_3.

Rate of entry of BMe_3 : 0·131 *mm./min.*

reaction occurs during the first 2½ mins., but, with the higher pressure of oxygen, a rapid reaction starts at about 3 mins., and the *p–t* curve soon becomes horizontal. Under these conditions the rate of contraction is the same as the rate of entry of trimethylboron to the reaction vessel. The fact that runs have been made which give a horizontal portion of the curve extending over a considerable period agrees with equation (1). With the lower pressure of oxygen, the rate is never sufficiently high to give a horizontal portion. It will be noticed that after about 13 mins. the slope of the curve begins to increase, indicating the deceleration of the reaction owing to consumption of the oxygen.

One sample of trimethylboron gave abnormal results. This produced long induction periods (*ca.* 10 mins.) terminated by a very rapid contraction. It seemed likely that this was due to some impurity in the alkyl. Since the latter had been prepared by the Grignard method, possible impurities were ether, methyl iodide, and boron trifluoride. It was found that none of these substances alone has any appreciable effect on the reaction. However, boron trifluoride together with a trace of water is a powerful inhibitor; for instance, pretreatment of the reaction vessel by admission of 10 mm. of water vapour and evacuation for 4 mins. introduced sufficient water to give strong inhibition with the trifluoride. Curves (3) and (4), Fig. 1, give results for runs in a pretreated vessel, in the presence of boron trifluoride. The technique in these runs consisted in pretreating the vessel as described above, and adding the fluoride and then the oxygen. Since a slow contraction occurred when the fluoride was admitted to the pretreated vessel (owing presumably to reaction between boron trifluoride and water) the pressures of trifluoride given in Fig. 1 are only approximate. After the mixture had stood for some time to ensure homogeneity, the trimethylboron was admitted. Curve 3 shows that little reaction occurred during the first 12 mins., but just after 15 mins. a very rapid reaction took place. In run (4) the admission of the alkyl was stopped after 11 mins. A slow reaction followed which gradually accelerated, and became quite rapid

at 29 mins. These results show that the inhibitor is gradually destroyed during a run, its removal being accompanied by acceleration of the reaction.

The above procedure is unsatisfactory for quantitative investigation, since the pressures of boron trifluoride and water cannot be measured accurately. The preparation of a mixture of known composition was therefore tried by the following method. Mixtures of water vapour and oxygen, and boron trifluoride and oxygen, were made in separate vessels and allowed to stand until homogeneous. Measured pressures of these were mixed in the reaction vessel together with oxygen, to obtain a mixture of the desired composition. The following mixtures were made up in the reaction vessel in this way :

Mixture.	A.	B.	C.	D.
H_2O (mm.)	0·02	0·14	0·31	0·17
BF_3 (mm.)	0·42	0·43	0·43	0·80
O_2 (mm.)	5·99	5·91	6·10	5·10

None of the mixtures gave any inhibition. The experiment with D was repeated, with the difference that an interval of 20 mins. was allowed to elapse between introducing the water–oxygen mixture into the vessel and adding the trifluoride–oxygen, and then a further period of 20 mins. before adding the necessary oxygen. In this case there was marked inhibition, reaction starting 9 mins. after the admission of trimethylboron was started. The inhibitor thus appears to be produced comparatively slowly by interaction between the trifluoride and water under these conditions. This is not so, however, when boron trifluoride is added to the pretreated reaction vessel, as in the earlier runs, and it is probable, therefore, that the inhibitor-producing reaction is a surface process.

Nothing is known about the chemical nature of the inhibitor except that it results from reaction between boron trifluoride and water : it might be HF, HBF_4, or a compound produced by the attack of HF on the reaction vessel. The following experiments show that the inhibitor is volatile. A run was carried out in which boron trifluoride was added to the pretreated reaction vessel; the latter was then evacuated for 4 mins. Oxygen was then let into the vessel, and trimethylboron was admitted as usual. There was no inhibition. In a further experiment, a bulb of about the same size as the reaction vessel was pretreated with water vapour, after which the trifluoride and oxygen were added. A reaction carried out with this mixture would have been subject to strong inhibition. The mixture was transferred to the dry reaction vessel, and trimethylboron admitted immediately. An induction period of 29 mins. was observed, showing that the inhibitor had been transferred with the gas mixture to the reaction vessel.

The last experiment lends some support to the view that the inhibition is a homogeneous process. If this were not so, it would have to be assumed that the inhibitor, initially formed by a surface process, in the mixing vessel, becomes desorbed and then readsorbed on the surface of the reaction vessel. The latter process, however, would be slow, since a large excess of oxygen was present. It will be seen later that experiments at higher pressures also point to homogeneous inhibition.

All the runs described so far, with the exception of the last, were repeated in a reaction vessel coated with paraffin wax. This produced no significant difference in the results.

If it is assumed that in Run 3 (Fig. 1) each molecule of BF_3 produces one of inhibitor, a value of 50 is obtained for the chain length. This is a minimum value.

(iii) *The Order of Reaction, and the Effect of Inert Gases.* The results given in Table I were obtained by admitting trimethylboron at a rate of about 0·1 mm./min. to the reaction vessel containing a known pressure of oxygen. When the desired pressure of alkyl had been reached, the admission was stopped, and pressure readings were taken at suitable intervals. Allowance was made for the amounts of reactants consumed during the admission of the alkyl by comparing the actual pressure change during admission with that calculated from the rate of entry of the alkyl.

TABLE I.

Reaction Rates in Waxed Reaction Vessels : Temperature 24·8°.

	Initial pressures, mm. $\times$ 10.		Initial rate of contraction,	
Run.	BMe_3.	O_2.	w, mm./min. $\times$ 100.	$100 \, w/[BMe_3][O_2]^2$.
1	1·38	29·0	2·80	2·41
2	0·97	29·7	1·84	2·15
3	1·46	15·35	0·735	2·14
4	2·70	15·36	1·52	2·39
5	2·89	7·76	0·38	2·18

TABLE II.

Reaction Rates in Unwaxed Vessel : Temperature 24·8°.

	Initial pressures, mm. $\times$ 10.		Initial rate of contraction,		
Run.	BMe_3.	O_2.	w, mm./min. $\times$ 100.	$100 \, w/[BMe_3][O_2]^2$.	$100 \, w/[BMe_3][O_2]$.
6	1·41	6·06	0·20	3·88	2·34
7	1·84	8·51	0·37	2·77	2·36
8	1·65	13·91	0·92	2·88	4·00
9	0·92	19·85	1·29	3·55	7·10
10	1·22	27·20	2·76	3·06	8·31
11	0·92	28·15	2·66	3·65	10·20
12	0·95	46·6	3·6	1·69	—
13	0·97	68·0	4·6	1·03	—
14	1·30	126·0	2·3	0·11	—

Table I shows that, in the range of pressures investigated, the rate is proportional to $[BMe_3][O_2]^2$. It is convenient to consider the runs in Table II in two groups; runs 6—11, which cover approximately the same pressure range as those of Table I, and 12—14 with considerably higher pressures of oxygen. With regard to the former group, the results, although not so satisfactory as those with the waxed vessel, seem to indicate that the rate follows a similar law, *i.e.*,

$$w = k[BMe_3][O_2]^2 \qquad \qquad (2)$$

The values for the proportionality " constant " obtained by assuming dependence on the first power of $[O_2]$ are recorded in col. 6. They show a very marked trend which is absent from the figures in col. 5. Runs 12, 13, 14 show that at higher

pressures of oxygen the rate increases much less rapidly than $[O_2]^2$: in fact increasing $[O_2]$ beyond a certain value causes a decrease in w (runs 13, 14). This is almost certainly a diffusion effect; it is readily understandable if the reaction starts on the walls. Under these conditions the rate of diffusion of trimethylboron to the walls may be less than the rate of the surface reaction, with the result that a region of lower alkyl concentration exists near the walls, and gives rise to a rate which is lower than would be expected. In agreement with this view is the fact that addition of a comparatively large pressure of nitrogen cuts down the rate markedly. Thus a mixture containing BMe_3 0·1, O_2 2·91, N_2 9·61 mm. gave $w = 1·24 \times 10^{-2}$ mm./min., whereas in the absence of nitrogen the rate is approximately $2·7 \times 10^{-2}$ mm./min. (run 11). A further effect noticed was that when comparatively high pressures of oxygen are used, the rate falls off more rapidly than would be expected during the course of a single run. This is also a diffusion effect.

The addition of moderate pressures of nitrogen has no measurable effect on the rate of reaction, as is evident from Table III.

TABLE III

Temperature 24·8°.

		Initial pressures, mm. $\times$ 10.		Initial rate of contraction,
Run.	BMe_3.	O_2.	N_2.	w, mm./min. $\times$ 100.
8	1·65	13·91	0	0·92
15	1·65	13·91	13·29	0·92
16	1·70	13·95	6·21	0·88

The absence of an inert-gas effect may be explained in a number of ways : (*a*) the reaction may be homogeneous, of the non-chain type, (*b*) it may be completely heterogeneous, (*c*) it may be a chain reaction in which chains begin and end on the walls, or (*d*) it may be a chain reaction in which chains begin and end, by a suitable mechanism, in the gas phase. The order of reaction, and the fact that ignition can be suppressed by an inhibitor eliminates (*b*), and the inhibition by

FIG. 2.

Reaction between trimethylboron and oxygen.
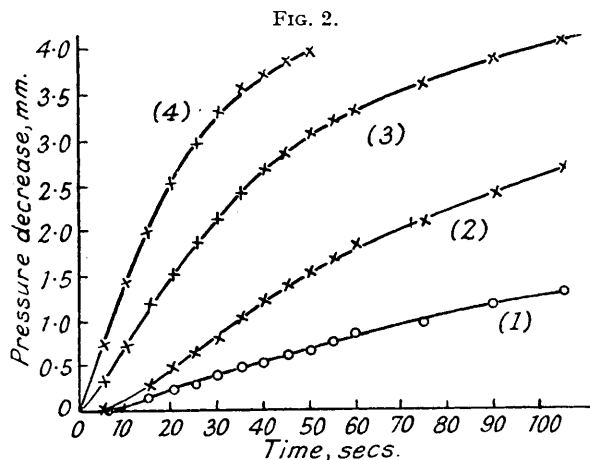
Initial pressures, mm.

	BMe_3.	O_2.		BMe_3.	O_2.
(1)	5·10	2·72	(3)	5·15	7·77
(2)	5·05	5·05	(4)	5·10	11·60

boron trifluoride–water mixture excludes (*a*). The effect of high pressures of oxygen or nitrogen in reducing the rate by impeding diffusion would appear to exclude (*d*), leaving (*c*) as the most probable alternative.

During the experiments described above, it was found that after the first few runs, reaction rates were satisfactorily reproducible. This is to be contrasted with the case of dimethylzinc, in which the solid oxidation products exert a strong catalytic effect.

(*b*) *The reaction at higher pressures.* (i) The Slow Reaction. The technique employed was similar to that described in Part II. The relations observed between total contraction and initial composition were the same as those described in section (*a*) (i) above, showing that the stoicheiometric reaction follows equation (1).

The pressure–time curves obtained are shown in Fig. 2, and the values of the maximum rate of contraction, w, are given in Table IV. The pressures of reactants given in the table correspond to the moment at which the rate is a maximum.

TABLE IV.

Temperature 25·0°.

	Pressures, mm.		w,		
Run.	BMe_3.	O_2.	mm./min.	100 $w/[BMe_3][O_2]^2$.	10 $w/[BMe_3][O_2]$.
1	4·6	2·2	0·94	4·2	0·93
2	4·1	4·1	2·4	3·5	1·43
3	3·9	6·5	5·2	3·2	2·05
4	4·3	10·8	11·1	2·2	2·40

From the figures in cols. 5 and 6 it would seem that the order of reaction with respect to oxygen is between 1 and 2—actually it is about 1·6. The value is only approximate, however, since the reacting mixture under the conditions of the experiment would almost certainly be inhomogeneous, especially at the higher pressures. Further, a rapid reaction would tend to maintain the inhomogeneity. Thus, the effect of the latter would probably be to retard the faster reaction

to a greater extent than the slower ones, *i.e.*, to lower the apparent order of reaction. It therefore seems reasonable to suppose that the true order with respect to oxygen is 2, as at lower pressures. The values for the ratio $w/[\text{BMe}_3][\text{O}_2]^2$ shown in Table IV, *viz.*, 2·2—4·2 × 10⁻², are in fact fairly close to the value obtained at lower pressures—*ca.* 3 × 10⁻² (Table II). A smaller reaction vessel was used in the present experiments, but if, as suggested earlier, chains begin and end on the walls, this would not affect the rate of reaction appreciably. The pressures given in Table IV are not very near to the ignition limit, so that branching would probably be small.

(ii) *Ignition.* A portion of the ignition boundary is shown in Fig. 3. There were no appreciable induction periods. It was noticed that with the higher pressures of trimethylboron, and pressures of oxygen only slightly above the limit, a rather feeble bluish flash was produced. Lower pressures of the alkyl, however, gave a very intense green flash. By plotting the minimum total pressures required for ignition against the corresponding values for the mol.-fraction of trimethylboron, it is seen that ignition occurs most readily with the mol.-fraction equal to 0·35.

(iii) *Inhibition.* It was found that if the reaction vessel was pretreated with water vapour as described earlier, addition of boron trifluoride raised the ignition limit slightly, *i.e.*, made the mixture less reactive. The amount of water introduced in this way was insufficient to cause marked retardation of the slow reaction. The following pressures of vapours were introduced into the reaction vessel, and the oxygen added rapidly : H_2O, 0·74; BF_3, 2·0; BMe_3, 7·7; O_2, 9·9 mm. An extremely slow reaction ensued, the rate of contraction being about 0·25 mm./min., whereas in the absence of inhibitor the rate would have been approximately 22 mm./min.

In another run the following pressures were used : H_2O, 0·74; BF_3, 0·9; BMe_3, 7·91; O_2, 47·0 mm. In this case also there was a very slow reaction. The pressures of alkyl and oxygen correspond to a point well inside the ignition region in the absence of inhibitor (see Fig. 3). Hence, both the slow and the explosive reaction are subject to inhibition.

FIG. 3.

Fig. 3.
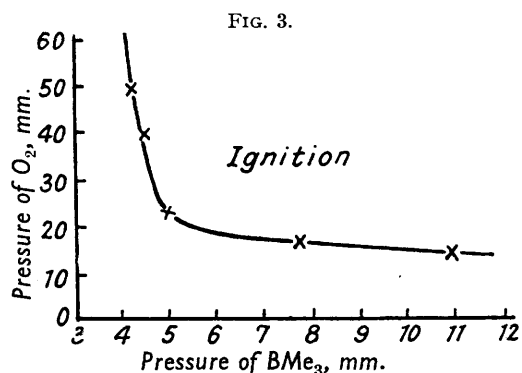
Ignition limits of trimethylboron and oxygen; spherical vessel, diameter 6 cm., 25°.

FIG. 4.
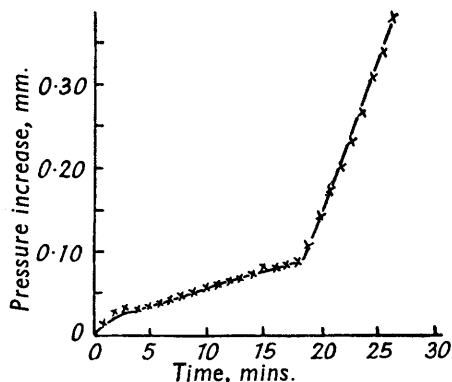
Admission of oxygen to tripropylboron. Initial pressure : 1·16 mm. BPr₃. Rate of entry of O_2 : 0·057 mm./min.

(2) *Tri-n-propylboron.*—The oxidation of this alkyl has only been briefly investigated. A typical pressure–time curve obtained at low pressure is shown in Fig. 4. The initial portion is almost horizontal; after a sharp " reversal " point the curve ascends steeply and almost linearly.

When the oxygen was stopped before the reversal point was reached no contraction occurred; further, the reaction mixture at this stage was rapidly and completely condensable in liquid air, showing that no appreciable pressure of oxygen was present. The pressures of oxygen added at the reversal point are very nearly equal to the initial pressure of the alkyl, as shown below :

Run	1	2	3	4
Initial press. of BPr₃, mm.	1·49	0·55	0·29	1·16
Pressure of O₂ added at reversal point, mm.	1·43	0·53	0·29	1·03

These facts suggest that the initial portion of the *p–t* curve corresponds to an oxidation following the equation

$$\text{BPr}_3 + \text{O}_2 \longrightarrow \text{BPr}_3\text{O}_2(g) \quad\quad\quad\quad (3)$$

proceeding at a rate which is always too fast to be measurable with the present technique. The small expansion before the reversal point may indicate the occurrence to a small extent of another reaction accompanied by an increase in volume.

The rate of increase of pressure after the reversal point was always considerably less than the rate of entry of oxygen (see Fig. 4). This may be due to a further slow oxidation of BPr₃O₂ to *n*-propyl borate.

Preliminary experiments with boron trifluoride–water mixtures indicated the existence of short induction periods showing that the oxidation of tripropyl- like that of trimethyl-boron is subject to inhibition.

(3) *Antimony Alkyls.*—The pressure–time curves obtained by the admission of oxygen to the vapours of trimethyl- and triethyl-stibine are shown in Figs. 5 and 6. It will be seen that, at the pressures used, oxidation of the former takes place at a measurable rate. In run (1) the pressure–time curve gradually decreases in slope as the oxygen accumulates in the reaction vessel; on stopping the oxygen after 20 mins. the contraction accompanying the reaction is clearly seen. In (2), at a higher pressure of trimethylstibine the *p–t* curve acquires a negative slope after about 8 mins. owing to the greater rate of reaction. The results for triethylstibine are quite different. On admitting oxygen even to low pressures of this alkyl, only a small initial rise in pressure is obtained, this soon giving way to a steady contraction (Fig. 6). At first sight this would appear to indicate a more rapid reaction with this alkyl. However, this is not necessarily so, since the cause of the reactions and the nature of the products might be different in the two cases. To test this point, a run was carried out with triethylstibine, in which the oxygen was cut off before reaching the reversal point (Curve 4, Fig. 6). Practically no further change in pressure occurred, showing that the stationary concentration of oxygen during the run must have been very small. This is in marked contrast to the result of a similar experiment with trimethylstibine (Curve 1, Fig. 5) and shows decisively that the rate of oxidation is much greater in the case of the ethyl compound. The reactions occurring during oxidation are probably complex. For instance, Dyke and Jones (*J.*, 1930, 1921) reported

that atmospheric oxidation of the higher antimony alkyls produced a mixture of R_3SbO, Sb_2O_3, and R_3SbO. In the present experiments no attempt was made to carry out a detailed analysis of the products. The oxidation of triethyl-stibine in the runs described above produced no gas which was not condensable in liquid air. The products had a strong smell of acetaldehyde, and gave a positive Schiff test for this. They appeared to mix completely with water, giving a faintly acid solution, and may have contained $SbEt_3O$ or $SbEtO(OH)_2$.

Fig. 5.
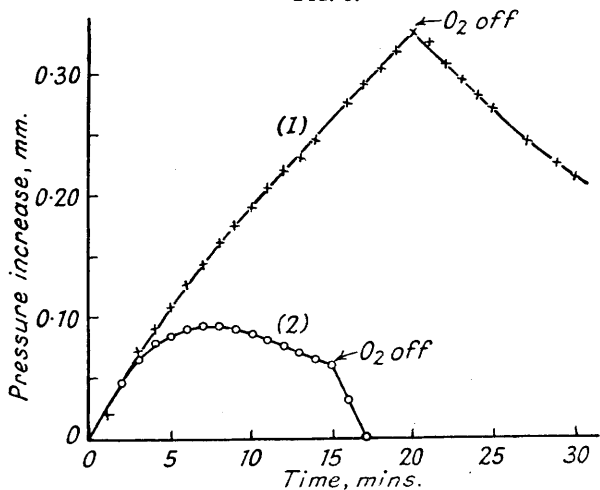
Fig. 6.

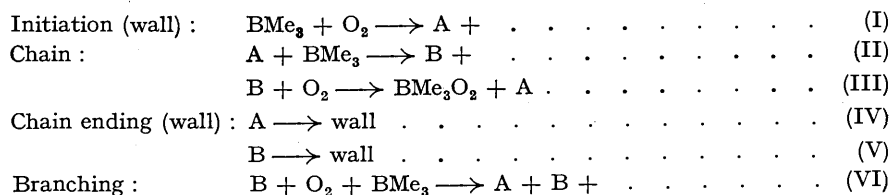*Initial pressures of* $SbMe_3$ *(mm.):* (1) 0·49, (2) 0·89.   *Rate of entry of* O_2 : 0·03 *mm./min.*
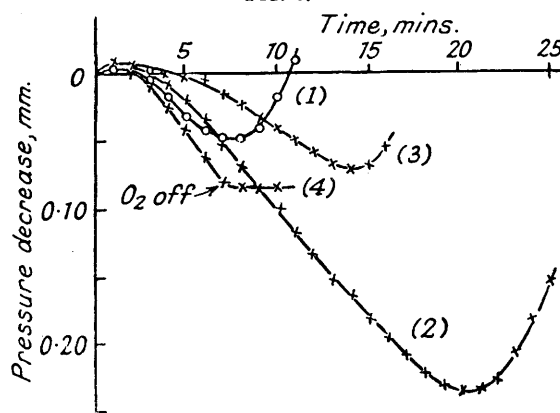
Admission of oxygen to triethylstibine.   Initial pressures of $SbEt_3$ *(mm.) :* (1) 0·24, (2) 0·56, (3) 0·44, (4) 0·60. *Rate of entry of* O_2 : 0·033 *mm./min.*

DISCUSSION.

1. *Kinetics.*—Since the homogeneous (explosive) oxidation of trimethylboron is subject to inhibition by boron trifluoride–water mixtures, it may be inferred that the oxidation is a chain process. This will be true whether the inhibitor functions in the gas phase or on the surface. It appears, however (p. 697), that the former is more probable. As mentioned on p. 698, the fact that moderate pressures of inert gas have no effect in the reaction rate suggests that chains begin and end on the walls under the conditions of the low-pressure experiments.

As in Part II, we may consider the general reaction scheme represented by equations (I)—(VI) :

Initiation (wall) : $BMe_3 + O_2 \longrightarrow A +$ . . . .   (I)

Chain : $A + BMe_3 \longrightarrow B +$ . . . .   (II)

$B + O_2 \longrightarrow BMe_3O_2 + A$ . . . .   (III)

Chain ending (wall) : $A \longrightarrow$ wall . . . .   (IV)

$B \longrightarrow$ wall . . . .   (V)

Branching : $B + O_2 + BMe_3 \longrightarrow A + B +$ . . . . . .   (VI)

Neglecting the consumption of BMe_3 in (I) and (VI), this gives for the rate of reaction :

$$-\frac{d[BMe_3]}{dt} = k_1f\{[BMe_3],[O_2]\} \frac{k_2k_3[BMe_3][O_2]}{k_2k_5[BMe_3] + k_3k_4[O_2] + k_4k_5 - k_2k_6[BMe_3]^2[O_2]} \quad . \quad . \quad (4)$$

where $k_1f\{[BMe_3],[O_2]\}$ is the rate at which the A centres formed by (I) leave the surface. If $k_1f\{[BMe_3],[O_2]\} = k_1[BMe_3][O_2]$, then on putting $k_4 = 0$ in (4) we obtain :

$$-\frac{d[BMe_3]}{dt} = \frac{k_1k_3[BMe_3][O_2]^2}{k_5 - k_6[BMe_3][O_2]} \quad . \quad . \quad . \quad . \quad . \quad (5)$$

which agrees with the experimental observation at low pressures, when the second term of the denominator is negligible in comparison to the first. Sufficient experimental data are not available to enable a comparison to be made with (5) at higher pressures.

The above scheme is similar to that given in Part II for the zinc alkyls, the differences being (*a*) the chain-breaking reaction is the destruction of " B " and not " A " at the walls, (*b*) a different form of expression is used for f, and (*c*) since BMe_3O_2 is the final product there is no need to include a reaction such as (VII), Part II. As with the zinc alkyls, we may obtain a radical chain by writing O and BMe_3O for A and B respectively, or an energy chain if we assume $A \equiv BMe_3O_2$ * and $B \equiv BMe_3$*.

A further possibility is that the initial encounter between the alkyls and oxygen produces $O_2 \rightarrow BMe_3$, which then reacts with BMe_3 to give $2BMe_2OMe$, probably in an excited state. The scheme then follows

equations (II), (III), (IV), (VI), with $A \equiv O_2 \to BMe_2 \cdot OMe$ and $B \equiv BMe_2 \cdot OMe$, and leads to an expression for the rate of reaction essentially the same as (5).

2. Reaction below Ignition Limit.—The zinc, boron, and antimony alkyls studied in these papers react rapidly at pressures considerably below the ignition limits. With the ethyl and the propyl derivatives the reactions are in fact always too fast to be readily measurable. In this respect these reactions differ markedly from many other oxidations, *e.g.*, those of hydrogen, phosphorus, phosphine, triethylphosphine (Semenoff, " Chemical Kinetics and Chain Reactions," Oxford, 1935) and silane (Eméleus and Stewart, *J.*, 1935, 1182), all of which exhibit an abrupt lower explosion limit, below which reaction is exceedingly slow. This difference is bound up with the nature of the primary chain. The rate of a chain reaction at low pressures may be expressed as $f(c)/(k - \delta)$, where $f(c)$ is a function of the concentration of reactants representing the rate of primary generation of centres, k determines the probability of chain breaking at the walls, and δ is the branching factor, which of course depends on the concentrations of reactants. If $f(c)/k$ is large, then the rate of reaction will be considerable even in the absence of branching. The condition for an isothermal explosion is $\delta = k$, so that it is quite possible in this case to have a fast reaction well below the ignition limit. In other words, the ignition limit will not be a reaction limit. This will usually also be true if a thermal explosion intervenes before $\delta = k$. On the other hand, if $f(c)/k$ is very small, δ will have to be almost equal to k if the rate is to be measurably fast, in which case a further small increase in pressure will normally be sufficient to give $\delta = k$. Thus the ignition limit will also be approximately a reaction limit.

These considerations are therefore consistent with the view that the rate of the primary chain reaction $(f(c)/k)$ is great in the case of the alkyls, and that branching is unimportant except near the ignition limit. In the other oxidations mentioned above the primary chain reaction is sluggish. It may be concluded that normally the range of pressures over which reaction occurs below the lower ignition limit is an indication of the probability of the primary (unbranched) chain reaction, a wide range corresponding to a high probability and *vice versa*. An exception to this will be the cases (unusual at low pressures) in which the branching and termination reactions depend on the pressures of reactants in a similar manner.

3. The Relative Rates of Oxidation of Methyl and Higher Alkyls.—The results described in this and the preceding paper show that the methyl compounds of zinc, boron, and antimony oxidise at a much slower rate than the ethyl and *n*-propyl derivatives. In all these oxidations a central atom–carbon bond is broken, and it is to be expected that the rate of reaction will be affected by changes in the bond energy of this link. The only relevant data on these bond energies are those of Dr. L. H. Long (unpublished), which show that the Zn–C bond in dimethylzinc is a few kg.-cals. stronger than that in diethylzinc. This change in bond energy is due to hyperconjugation and is produced by additional resonance in the higher aliphatic radicals according to the ideas first expressed by Wheland (*J. Chem. Physics*, 1934, **2**, 474) and Baker and Nathan (*J.*, 1935, 1844) and developed by Polanyi and his co-workers (see, *e.g.*, Baughan, Evans, and Polanyi, *Trans. Faraday Soc.*, 1941, **37**, 377; Butler and Polanyi, *ibid.*, 1943, **39**, 19). For example, in the ethyl radical, $CH_3 \cdot CH_2 \cdot$ and the three

structures of the type $H - \overset{H}{\underset{H}{C}} = CH_2$ contribute, while in *n*-propyl and higher radicals there are probably further

resonating structures. As a consequence there may be a fall in the bond energy from CH_3-X to C_2H_5-X provided the increase in resonance energy of the radical is not outweighed by the increasing interaction between the ionic and homopolar states of RX which is due to the resonance of R ions, and which increases from CH_3 to C_2H_5. Such a fall in bond energy has been observed by Butler and Polanyi (*ibid.*) in a series of organic iodides; presumably the same effect is operative in the alkyls of zinc, boron, and antimony. As there is in fact a falling off in the strength of the Zn–C bond as one passes from the methyl to the ethyl, it is likely that there will be a similar effect with the boron and antimony compounds, since the ionic contributions will be smaller in the derivatives of these elements than in those of zinc.

It is noteworthy that the odour of zinc compounds probably gives a qualitative indication of the rapidity with which they oxidise in the air. Thus the methyls have a pungent and characteristic smell, while the higher alkyls are practically odourless. Further, the decrease in spontaneous inflammability which accompanies an increase in molecular weight must be due to the corresponding decrease in vapour pressure.