

143. Physical and Chemical Properties of Organo-metallic Compounds. Part II. The Oxidation of Zinc Alkyls.

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The kinetics of the oxidation of dimethyl-, diethyl-, and di-*n*-propyl-zinc have been studied. The technique used at low pressures consisted in the observation of pressure changes occurring when one reactant was admitted slowly to the other. It has been found that the methyl derivative oxidises more slowly than the higher alkyls. Oxidation ceases with the formation of $ZnMe_2O$, whereas with the higher alkyls ZnR_2O_2 may be formed. The reaction with the dimethyl is shown to be a chain process starting and ending on the walls. It is strongly catalysed by the solid reaction products. Possible mechanisms are discussed.

THE kinetics of the oxidation of the zinc alkyls have been studied as part of a programme of work on spontaneously inflammable alkyls. The only previous measurements of this kind were made by Thompson and Kelland (J., 1933, 746) on dimethyl- and diethyl-zinc. These authors found that in the gas phase at low pressure a reaction of measurable rate occurs between the dimethyl and oxygen, leading to the formation of solid methylzinc methoxide, $ZnMe \cdot OMe$. It was concluded that the reaction velocity is proportional to the pressure of the dimethyl and independent of the oxygen pressure. The addition of inert gas or a change in vessel diameter produced practically no change in rate. At higher pressures explosion was observed, the explosion limits being raised by a decrease in vessel diameter, by the addition of inert gas, or by a decrease in temperature. These results were considered to indicate a chain mechanism, which, however, was not discussed in detail by Thompson and Kelland.

The results of the present paper extend those of Thompson and Kelland to lower pressures, by the use of a different technique. In the main the earlier results are confirmed. It has been found, however, that the reaction rate is very markedly increased by the presence of solid reaction products. Further, at pressures near the ignition boundary, the rate is dependent upon the oxygen pressure, and is depressed by the addition of inert gas. It is shown later that the kinetic results are consistent with a chain mechanism in which chains start and end on the wall.

In a second paper Thompson and Kelland (J., 1933, 756) described their results with diethylzinc. They found that with this alkyl oxidation proceeds to the second stage ($ZnEt_2O_2$). The reaction was stated to be much slower than that of the dimethyl; in particular, ignition could not be obtained. The present results conflict with these observations and show that oxidation of $ZnEt_2$ can lead to $ZnEt_2O$ or $ZnEt_2O_2$ according to the conditions. Further, oxidation appears to be too fast to allow measurement, even down to the lowest pressures, and ignition occurs even more readily (*i.e.*, at lower pressures) than with $ZnMe_2$.

Dipropylzinc resembles the diethyl in undergoing an extremely rapid oxidation. Thus the oxidation of dimethylzinc differs from that of the higher alkyls in that under similar conditions it is a much slower process. A similar phenomenon occurs with the alkyls of the other elements studied (boron, antimony), and is discussed in Part III of this series.

All the alkyls investigated oxidise rapidly at pressures far below the lower ignition limits. In this respect these oxidations differ from many other chain reactions in which the transition between very slow reaction and ignition occurs abruptly over a comparatively small pressure range. The kinetic implications of this behaviour are discussed in Part III.

EXPERIMENTAL.

(A) *General Technique for Investigation of Reactions at Low Pressures.*—The method consists in the observation of the pressure changes which occur when one reactant is slowly admitted to the other in a thermostated reaction vessel. Usually oxygen was admitted to the vapour of the alkyl, at pressures of alkyl up to a few mm. The oxygen was stored in a large bulb at approximately atmospheric pressure. Its rate of admission was controlled by a capillary leading to an inlet tube which terminated near the centre of the reaction vessel. The latter was spherical, with diameter 8 cm., and was immersed in a thermostat which was usually kept at $25.0^\circ \pm 0.1^\circ$. The reaction vessel communicated with a manometer containing concentrated sulphuric acid through a capillary about 30 cm. long and of 0.5 mm. internal diameter. A travelling microscope with micrometer eyepiece allowed pressure changes of 0.01 mm. to be read with ease. In some cases a small amount of reaction between the acid and the alkyl vapour occurred, leading to initial instability of the manometer. This disappeared after short standing, as the small quantity of permanent gas produced exerted a strong buffering action in the capillary tube between the reaction vessel and manometer. The admission of oxygen was not started until the pressure had been steady for a few minutes. The alkyl was stored in a small trap at -80° . This was frequently evacuated to prevent accumulation of decomposition products. When it was decided to admit the vapour of the alkyl to oxygen in the reaction vessel, the liquid was first vaporised into a storage bulb.

The whole apparatus could be evacuated by a three-stage mercury diffusion pump and a Hyvac pump. In addition, a Toepler pump enabled gaseous products to be withdrawn for analysis.

Fig. 1 illustrates some features of the pressure-time ($p-t$) curves obtained. Actually, it is typical of the curves given by diethylzinc. The initial pressure of the alkyl is taken as the zero of pressure in the diagram. If no reaction occurred, the pressure-time curve would be the straight line OA , representing the entry of oxygen to the reaction vessel at a constant rate. Actually, reaction is accompanied by a reduction in volume, and on admission of oxygen the total pressure falls, as indicated by OB . The rate of contraction at any moment is given by the difference in the slopes of OA and the $p-t$ curve. At the "reversal point" B , the rate of contraction just equals the rate of admission of oxygen, and the $p-t$ curve is parallel to the time axis. After B is passed, the rate of contraction is less than the rate of admission of oxygen, and the pressure begins to increase. Eventually, when reaction is complete, the $p-t$ curve becomes parallel to OA . The total contraction due to reaction of the initial pressure of the alkyl is then given by the final value of the vertical distance ab . If it can be assumed that the course of the reaction does not change as the experiment proceeds, this enables rates of contraction to be transformed into rates of reaction.

The $p-t$ curve does not always start off with a negative slope. If the reaction is very slow, as in the case of dimethylzinc, the initial portion of the curve may be indistinguishable from OA (see, e.g., Fig. 3). In such cases it is convenient, after admitting the oxygen for a known time, to cut off the gas, and follow the pressure changes.

The "sharpness" of the curve near the reversal point is an indication of the rate of reaction—a rapid reaction leading to a sharp reversal point, and *vice versa* (cf. Figs. 1 and 3).

In studying these reactions at low pressures it is often difficult to decide whether one is dealing with a partly or wholly homogeneous, or a completely surface process. Since a number of alkyls produce non-volatile solids on oxidation, this point could frequently be decided by using the Tyndall beam phenomenon. On focusing a cone of light from a carbon arc into the reaction vessel it was often possible to observe the formation of solid particles in the gas phase, and to distinguish the zone of precipitation fairly clearly. Detailed descriptions of the phenomena observed are given below.

(B) *Reactions at Higher Pressures.*—A spherical reaction vessel, 6 cm. in diameter, immersed in a water thermostat at $25^\circ \pm 0.1^\circ$ was used in these experiments. Pressures were measured by a glass Bourdon gauge, reading to 0.03 mm. of mercury. After the desired pressure of the alkyl had been admitted, a known pressure of oxygen was added as quickly as possible, by momentarily opening a tap leading to a measuring vessel containing oxygen. The pressure of oxygen entering the reaction vessel was calculated from the decrease in pressure in the measuring vessel.

Generally, the reaction vessel was cleaned between runs by washing with dilute nitric acid and distilled water. This treatment was found to lead to reproducible results.

(C) *Preparation and Purification of Materials.*—

(i) *Alkyls.* The preparation and purification of the alkyls have been described in Part I (this vol., p. 468). (ii) Oxygen was taken from a cylinder, passed over heated platinised asbestos, and condensed in a trap in liquid nitrogen. The liquid was then allowed to vaporise slowly, the first and the last third being rejected. (iii) Nitrogen was obtained from a cylinder, passed through a liquid-air trap, and used without further purification. (iv) Carbon dioxide was also obtained from a cylinder, frozen in liquid air, and fractionated in a vacuum.

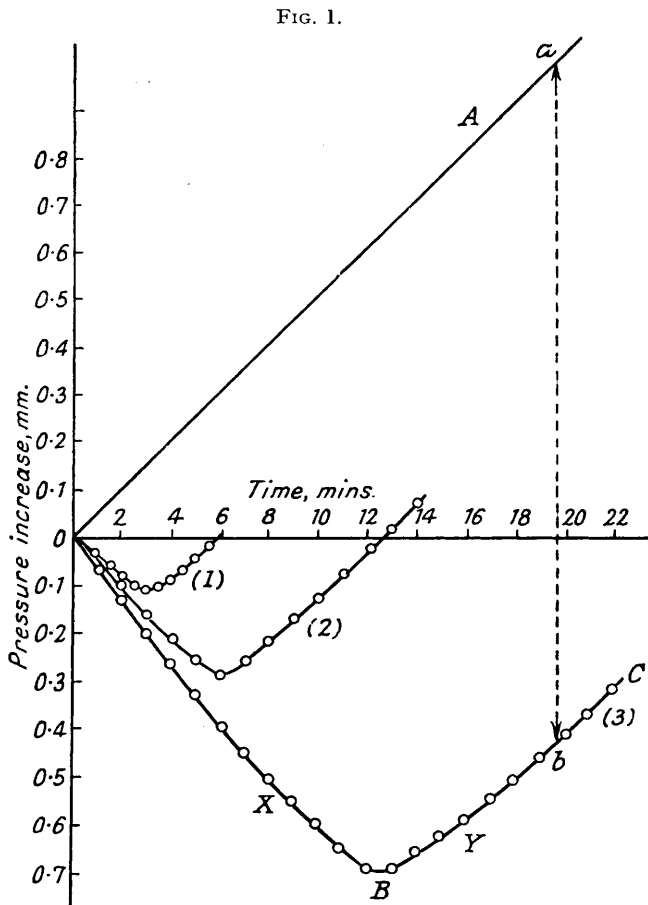
(D) *Results.*

(1) *Diethylzinc.*—(a) *The reaction at low pressures.* A series of $p-t$ curves obtained by admitting oxygen to diethylzinc vapour is shown in Fig. 1. In these experiments the reaction vessel was washed with dilute nitric acid and distilled water before each run.

The rate of entry of oxygen was in all cases 0.052 mm./min. In addition to these experiments, further runs were carried out with lower pressures of the alkyl, the lowest used being 0.02 mm. with a rate of admission of oxygen of 0.004 mm./min. In these runs an immediate contraction followed the addition of oxygen, the $p-t$ curves being similar to those of Fig. 1. Thus, at pressures of diethylzinc greater than 0.02 mm. the reaction is too fast to be measured with this technique. Data obtained from the $p-t$ curves are collected in Table I.

The $p-t$ curve for run 4 is omitted from Fig. 1 for the sake of clarity; it follows that of run 3 very closely.

In runs 6 and 7 (Table I), the oxygen was stopped shortly after the reversal point had been passed, and the volatile products were then fractionated and analysed (Table II).



Admission of oxygen to diethylzinc. Initial pressures of $ZnEt_2$: (1) 0.21 mm., (2) 0.45 mm., (3) 0.95 mm.

TABLE I.

No. of run.	Initial p_{ZnEt_2} (mm.).	Initial slope, mm./min.	O_2 added at reversal point (mm.).	Total contraction	
				$\frac{O_2}{p_{ZnEt_2}}$	p_{ZnEt_2}
1	0.21	0.044	0.16	0.78	1.47
2	0.45	0.059	0.3	0.67	1.46
3	0.945	0.069	0.61	0.65	1.46
4	0.99	0.069	0.63	0.64	1.45
5	2.53	0.081	1.52	0.60	1.40
6	2.54	0.081	—	0.60	1.38
7	3.62	—	—	0.59	1.34

Four runs (8, 9, 10 and 11) in which the reactants were mixed in the reverse order (*i.e.*, alkyl admitted to oxygen) gave $p-t$ curves of the same general shape as those of Fig. 1. Data from these experiments are given in Tables II and III.

Analysis of the volatile products in run 11 gave results similar to those obtained in 6 and 7 (see Table II).

An inspection of the $p-t$ curves of Fig. 1 shows that the portions OB , BC , are not straight lines over their whole length: OB starts off in a rectilinear manner, but eventually at X begins to become slightly concave to the time axis. Similarly, BY is slightly concave, but the curvature rapidly diminishes and soon disappears. If the oxygen is cut off in

TABLE II.

No. of run.	Initial pressures, mm.	Products (mm.).			Total hydrocarbon
		Unsaturated hydrocarbon.	C ₂ H ₆ .	C ₄ H ₁₀ .	$\frac{p_{ZnEt_2}}{p_{ZnEt_2}}$
6	2.54 } ZnEt ₂	0.21	0.15	0.20	0.22
7	3.62 }	0.30	0.27	0.33	0.25
11	2.01 O ₂	0.15	0.20	0.13	0.24

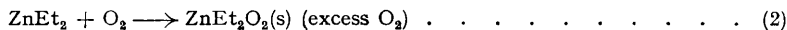
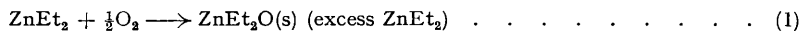
TABLE III.

No. of run.	Initial p _{O₂} (mm.).	ZnEt ₂ added at reversal point (mm.).	O ₂		Total contraction
			$\frac{p_{ZnEt_2}}{p_{ZnEt_2}}$	$\frac{p_{ZnEt_2}}{p_{ZnEt_2}}$	$\frac{p_{ZnEt_2}}{p_{ZnEt_2}}$
8	0.50	0.49	1.02		1.82
9	0.51	0.46	1.11		1.90
10	0.95	0.97	0.98		1.93

the ranges OX or YO no further contraction occurs, whereas in the ranges XB, BY, a slow contraction continues for a short time after stopping the oxygen. The curvature is thus due in part to the retardation in the diffusion of the gases in the range XBY, produced by the hydrocarbon formed during the reaction. In the main, however, the curvature of the $p-t$ curve is probably due to a change in the course of the reaction as the pressure of diethylzinc decreases (see below). The point to be emphasised here is that only a very small amount of reaction occurs when the oxygen is stopped. This, together with the fact that rapid reaction occurs down to pressures of diethylzinc as low as 0.02 mm., shows that the reversal point must be close to the "end-point" of the reaction. The relative volumes of oxygen and alkyl reacting, as calculated from the reversal points, are given in col. 5 of Table I for runs 1-5, while col. 6 gives the ratio of the total contraction to the initial diethylzinc pressures. In the case of runs 6 and 7, the ratios are calculated from the analyses of the products after addition of excess oxygen to the alkyl. It will be seen that the figures for these runs fit into the general series of values obtained from the reversal times.

Table III gives similar ratios for the runs in which the reactants were mixed in the reverse order.

Course of reaction. Table I shows that for the higher pressures of diethylzinc, reaction is complete when the pressure of oxygen added is rather greater than half the initial pressure of the alkyl (see col. 5). On the other hand, when oxygen is present initially and the alkyl is added, it appears that approximately equal pressures of the compounds react (Table III, col. 4). Since only comparatively small quantities of gaseous products are formed, this suggests that the main reactions are as follows:



In agreement with this are the following facts:

(i) From Table I it appears that, as the initial pressure of diethylzinc increases, the pressure of oxygen reacting with a given pressure of the alkyl diminishes steadily. This would be expected, since with a constant rate of admission of oxygen, the lower the pressure of the alkyl the more important reaction (2) becomes.

(ii) The initial slope of the $p-t$ curve increases as the initial pressure of diethylzinc increases. This again may be attributed to an increase in the relative importance of (1) under these conditions, since for a given addition of oxygen, this reaction will lead to the greater contraction.

During the course of a single run in which oxygen is added to the alkyl, (1) will steadily decrease in importance relative to (2). This will lead to the curvature of the $p-t$ curves observed experimentally (see also above).

It may be noted that Thompson and Kelland (*loc. cit.*) concluded that equal pressures of the reactants take part, with formation of solid ZnEt₂O₂. They did not identify reaction (1).

The hydrocarbons are probably formed from ethyl radicals, which result from collisions between the alkyl and hot molecules of products, *e.g.*, ZnEt₂O₂. In agreement with this it was found that the more rapidly the oxygen was added the greater the yield of hydrocarbons. Thus values for the ratio hydrocarbon/ZnEt₂ up to 1.3 may be obtained for fairly rapid additions. At the same time the solid product, instead of being white, acquires a darker colour and contains free zinc.

The Tyndall beam. On focusing a beam of light into the reaction vessel, it was found that the Tyndall beam becomes evident almost immediately the admission of the oxygen starts. For moderate diethylzinc pressures (*ca.* 1 mm.) there is a zone surrounding the oxygen inlet where the beam is invisible. This zone, in which there is little precipitation of solid, probably contains mainly oxygen, since the alkyl vapour has to diffuse against the oxygen stream. The oxygen may sweep out the solid particles mechanically, or alternatively the nuclei may not have sufficient time to grow to a size suitable for producing the beam during their stay in this region. Surrounding the central zone is a region of strong precipitation becoming feebler towards the wall of the vessel. As the initial pressure of diethylzinc increases, the central zone and the zone of precipitation contract, until at 10 mm. the precipitation region alone is visible as a line extending from the inlet tube. The Tyndall beam disappears sharply at the reversal point of the $p-t$ curve, suggesting that the particles producing it rapidly coalesce and/or settle on the walls. These experiments provide strong evidence for the occurrence of a homogeneous gas reaction and suggest that the main reaction is homogeneous. At very low pressures of diethylzinc—*ca.* 0.05 mm.—no Tyndall beam could be obtained. This is probably due to the extremely low stationary concentration of particles formed in these circumstances. Thus there is no proof that the reaction is homogeneous at these low pressures, but there is no reason to believe it heterogeneous.

A number of experiments were carried out without the beam of light to ascertain whether any luminescence occurred during reaction. None could be observed. This applies also to dimethyl- and dipropyl-zinc.

(b) *The reaction at higher pressures.* When a sufficiently high pressure of oxygen is added to diethylzinc at pressures above about 4 mm. ignition occurs, accompanied by either a red or a blue flash, depending on the pressure of oxygen. Higher pressures give blue flashes. In some cases, with intermediate oxygen pressures, both kinds of flash were observed simultaneously, the blue being near the centre of the reaction vessel, and surrounded by the red. Fig. 2 shows the ignition limits. The "hatched" area in the diagram represents the region of pressure in which both types of flash are observed together. No spectroscopic observations of these flashes have been made. It is interesting to note, however, that the ignition emission spectrum of zinc contains two strong lines in the visible, situated at 6103 and 4912 Å. respectively, which may be responsible for the red and the blue flashes.

A similar curve has been obtained by using dry air instead of oxygen. In this case only red flashes can be obtained. Ignition is always accompanied by the formation of a black deposit containing metallic zinc on the reaction vessel.

These results are in disagreement with those of Thompson and Kelland. The cause of the discrepancy is not clear. Since Thompson and Kelland worked at about 50° and noted a considerable amount of attack by the alkyl on the tap grease used, it is possible that the diethylzinc vapour became contaminated in their experiments.

(2) *Dimethylzinc*.—(a) *The reaction at low pressures*. (i) *Determination of Ratio of Reactants*. Preliminary investigations showed that the reaction between dimethylzinc and oxygen is comparatively slow, with the result that there is no well-defined reversal point in the $p-t$ curve. It is therefore necessary to determine the relative pressures reacting by another method.

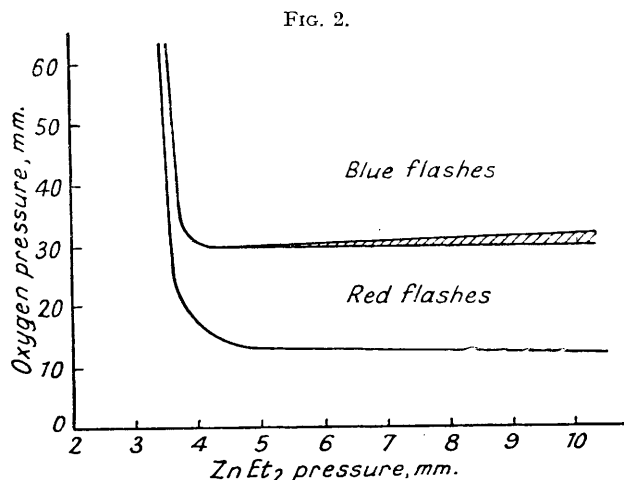
Oxygen was admitted at a known rate to the reaction vessel containing the alkyl vapour at a known pressure. After about $\frac{1}{2}$ hour's standing no further change in pressure occurred. The products were separated by low-temperature fractionation, and analysed. The results of a typical experiment are given below, all pressures being given in mm.:

Initial pressure ZnMe ₂	6.35	Final mixture consisted of		
O ₂ added	1.37	CO	0.10	C ₂ H ₆
Final pressure	4.20	CH ₄	0.70	ZnMe ₂
				0.08
				3.30

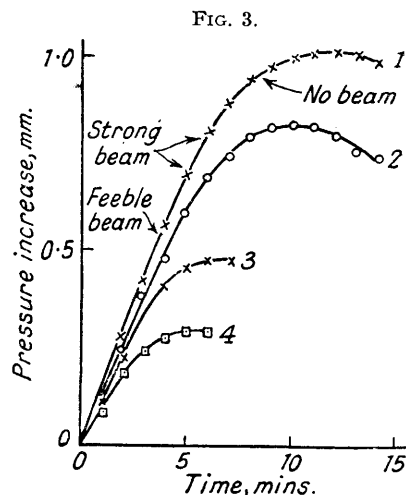
A white non-volatile solid was formed during reaction. From the above experiment it is seen that 3.05 mm. of the dimethyl react with 1.37 mm. of oxygen, giving a contraction of 3.52 mm. This agrees with the main reaction



According to this, the ratios O₂/ZnMe₂ and contraction/ZnMe₂ should have values of 0.5 and 1.5 respectively, whereas in the above experiment the values are 0.45 and 1.15. The discrepancies are probably due to the formation of carbon



Ignition limits of diethylzinc. Spherical vessel, diam. 6 cm., 25°.



Oxidation of dimethylzinc: Effect of products on reaction rate. Initial pressure of O₂: 10 mm. Rate of entry of ZnMe₂: 0.154 mm./min.

monoxide and hydrocarbons. The latter correspond to the decomposition of 0.45 mm. of dimethylzinc, or about 14% of the total (reckoned on a carbon basis), leaving 2.62 mm. of alkyl to react with 1.37 mm. of oxygen, according to (3), if it is assumed that no oxygen enters into the reaction forming hydrocarbons.

A few runs were done at higher pressures, about 50 mm. of oxygen being rapidly added to approximately 6 mm. of dimethylzinc in the reaction vessel. Under these conditions it was found that practically no ethane was formed but the volume of methane increased, and corresponded to 15–17% of the alkyl oxidised. In these experiments, in which the initial mixture was close to the ignition limit, it seems that (3) still represents the main reaction.

A second series of experiments was done in which (excess of) oxygen was present initially in the reaction vessel. The following results (pressures in mm.) are typical of this series.

Initial pressure O ₂	10.65	Final mixture consisted of		
ZnMe ₂ added	10.75	O ₂	4.86	CH ₄
Final pressure	6.83	CO	0.32	C ₂ H ₆
				0.68
				0.67

Thus 10.75 mm. of alkyl react with 5.79 mm. of oxygen to give the solid product together with the relatively small quantities of hydrocarbons and carbon monoxide. In this case also it is therefore clear that (3) represents the main reaction. The carbon monoxide and hydrocarbons correspond to 1.18 mm. of dimethylzinc, on a carbon basis, *i.e.*, about 11% of the total alkyl reacting.

These results show that even when excess of oxygen is employed, oxidation of dimethylzinc, unlike that of the diethyl compound, occurs only to the first stage, ZnMe₂O.

(ii) *Pressure-Time Curves*. The effect of surface. Although reaction is accompanied by contraction, an initial increase in pressure was always obtained on admitting dimethylzinc to oxygen (see Fig. 3). During the first few minutes reaction is extremely slow, but as the pressure of the alkyl builds up the rate increases, and the slope of the $p-t$ curve becomes negative. These results are in marked contrast to those obtained with diethylzinc.

It was found that the solid product which accumulates during a run strongly catalyses the reaction. In this respect the latter resembles the oxidation of monogermene (Emeléus and Gardner, *J.*, 1938, 1900). This effect is shown by Fig. 3. Curve 1 was obtained with the reaction vessel initially clean, while curves 2, 3, 4 refer to successive runs made without cleaning the vessel. A coating of paraffin wax on the inside of the vessel had no effect on the $p-t$ curve.

The usual method of investigating the effect of surface, by packing the vessel with glass beads, was inapplicable in

this case, as it would interfere with the mixing of the gases. Attempts were made to obtain further information by using a smaller reaction vessel. Reproducible results could not be obtained with this, however. On examination it was found that the solid product was deposited in patches on the surface and not uniformly as with the larger vessel. The non-reproducibility was probably bound up with this.

The effect of foreign gases on the reaction rate. The addition of nitrogen was found to have little effect on the rate of reaction; the tendency was, however, to increase it slightly. The addition of the vapours of methyl or ethyl iodide was also without appreciable effect on the reaction rate.

The order of reaction. The strong catalytic effect of the solid products makes the determination of the order of reaction difficult and uncertain. The method used consisted in starting with a known pressure of oxygen in the reaction vessel, adding dimethylzinc for a known time, then stopping the alkyl and observing the pressure changes. In all cases the rate of reaction was extremely slow, and it is considered that the initial rate of contraction corresponds to that in a clean vessel. It was found that the rate of reaction in any one run remained almost constant for a period longer than would be expected. This was probably due to the increase in rate due to contamination of the walls approximately balancing the decrease due to consumption of the reactants. Results are given in Table IV.

TABLE IV.

Initial pressure of O ₂ = 1.62 mm.			
Initial pressure, <i>p</i> , of ZnMe ₂ , mm.	Initial rate of contraction, <i>w</i> , mm./min. × 100.	100 <i>w</i> / <i>p</i> ² .	100 <i>w</i> (mm./min.) calc. from eqn. (8).
0.23	0.32	6.05	0.32
0.34	0.55	4.76	0.69
0.51	1.15	4.41	1.56
0.62	1.79	4.66	2.30
0.68	2.39	5.16	2.77

These results, with perhaps the exception of that at the lowest pressure, are very roughly in agreement with a bimolecular law, as shown in col. 3. As far as could be ascertained, the reaction is of zero order with respect to oxygen.

FIG. 4.

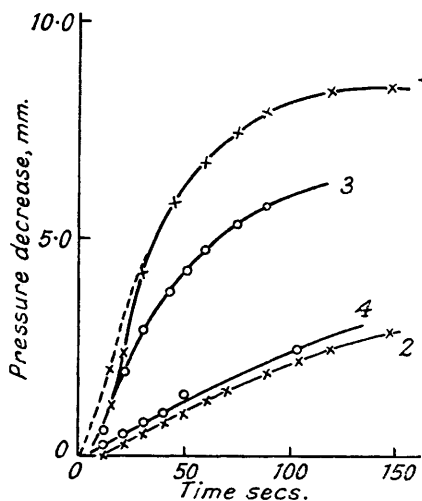
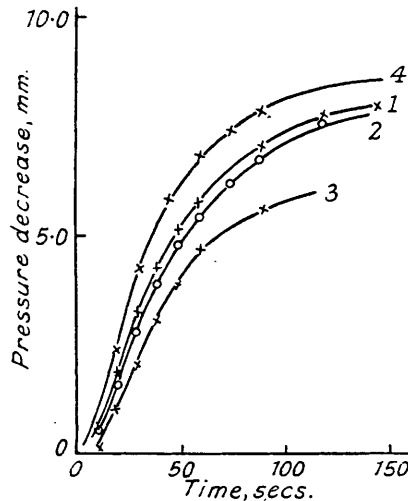


FIG. 5.



Reaction between dimethylzinc and oxygen: pressures in mm.

- (1) ZnMe₂, 7.50; O₂, 30.8. (2) ZnMe₂, 3.85; O₂, 32.9.
(3) ZnMe₂, 7.50; O₂, 13.4. (4) ZnMe₂, 3.90; O₂, 15.3.

Effect of foreign gases on rate of oxidation of dimethylzinc: pressures in mm.

- (1) ZnMe₂, 7.55; O₂, 34.5; N₂, 9.4. (2) ZnMe₂, 7.50;
O₂, 31.0; N₂, 22.2. (3) ZnMe₂, 7.50; O₂, 31.8; CO₂,
30.5. (4) ZnMe₂, 7.50; O₂, 30.8.

In a "dirty" reaction vessel the reaction was of first order with respect to dimethylzinc, and of zero order with respect to oxygen. The velocity constant, obtained by plotting $\log [\text{ZnMe}_2]$ against time, has the value 0.034 min.^{-1} .

The Tyndall beam. Starting with oxygen in the reaction vessel, no beam could be obtained on admitting dimethylzinc unless the initial pressure of oxygen was above 3 mm. With higher pressures (10 mm.) the beam became visible after a few minutes and was fairly strong. It gradually faded, however, and finally disappeared (see Fig. 3). It is interesting that an increase in the pressure of oxygen enables a beam to be obtained, although it does not increase the rate of reaction.

Increasing the total pressure can assist precipitation by impeding diffusion to the walls. The disappearance of the beam may be explained if the condensation of vapour on the walls occurs much more readily when the latter have become coated with a solid film of product. Initially, with a comparatively high gas pressure, sufficient supersaturation is produced over a considerable volume of the vessel to cause precipitation of fine particles. These will then grow as the reaction proceeds, and will probably coalesce to some extent and settle on the walls. Any further deposition will then take place mainly on the walls, since the reaction is too slow to permit any appreciable supersaturation to be formed. In agreement with this, it was found that no beam can be obtained in a vessel in which a run has previously been carried out. The only alternative explanation is that in a dirty vessel the reaction is very largely heterogeneous. This is not acceptable, however; Fig. 3 shows that in a clean vessel a beam appears when about 0.5 mm. of dimethylzinc has been admitted. Now, in a dirty vessel pressures of this alkyl of 0.5 mm. may readily be reached. Thus, unless the presence of the solid on the walls of the reaction vessel suppresses the gas phase reaction (which seems very unlikely) this cannot be the true explanation.

(b) *The reaction at higher pressures.* The method used was similar to that described for the diethyl. Results are

shown in Figs. 4 and 5. Curves 1, 2, 3, and 4 of Fig. 4 are typical of runs carried out in a clean reaction vessel. At the higher pressures of dimethylzinc (curves 1 and 3) there is a short induction period, after which the reaction accelerates very markedly and then dies away. At the lower pressure of the alkyl (curves 2 and 4) there still appears to be an induction period, although the subsequent acceleration is less marked. A comparison of curves 1 and 3 shows that, when $p_{\text{ZnMe}_2} = 7.5$ mm., the maximum rate is dependent upon the oxygen pressure, while curves 2 and 4 show that when $p_{\text{ZnMe}_2} \sim 3.9$ mm., a considerable change in the pressure of oxygen has little effect on the rate (see also Table V). A series of runs with $p_{\text{ZnMe}_2} = 3.9$ mm. and pressures of oxygen intermediate between those used in runs 2 and 4 confirmed this result.

TABLE V.

Run.	Pressure (mm.) of reactant at maximum rate.		Maximum rate of contraction, mm./sec.	Calc. rate of contraction from eqn. (8), mm./sec.
	ZnMe ₂ .	O ₂ .		
1	6.20	30.3	0.37	0.37
2	3.85	32.9	0.024	0.023
3	6.76	13.1	0.13	0.11
4	3.90	15.3	0.024	0.019

Curve 5, the first portion of which is shown as a broken line in Fig. 4, was obtained with a dirty reaction vessel, using the same pressure as in run 1. The effect of the dirty surface is to remove the induction period completely, without producing any significant change in the maximum rate.

If the reaction follows the same course as in the low-pressure experiments, the total contraction with excess of oxygen present should be given by $[\text{ZnMe}_2]/0.74$. The final contractions in the runs shown in Fig. 4 tended to approach this value.

The effect of foreign gases. Both nitrogen and carbon dioxide were found to reduce the rate of reaction to some extent, the latter being considerably more effective than the former. The curves are shown in Fig. 5.

Ignition. When suitable pressures of dimethylzinc and oxygen are mixed, ignition occurs, accompanied by a blue flash. In contrast to the results with the diethyl compound, no red flashes could be obtained. Near the ignition limit there is an induction period of a few seconds. The whole of the ignition curve was not determined. With $p_{\text{ZnMe}_2} = 8.4$ mm., the limiting pressure of oxygen was found to be 45.0 mm. This is considerably higher than the limiting pressure for the same pressure of diethylzinc—ca. 12 mm.—in agreement with the slower oxidation of the methyl compound. This ignition limit was not changed when a dirty reaction vessel was used.

It may be noted that the pressures in run 1 (Fig. 4) are not very far removed from the ignition limits.

(3) *Oxidation of Mixtures of Dimethyl- and Diethyl-zinc.*—An investigation of the oxidation of these mixtures showed that the rate of reaction of the former with oxygen is not increased by addition of the latter alkyl. It may be concluded that active centres produced by the interaction of diethylzinc and oxygen react more readily with diethyl- than with dimethyl-zinc, *i.e.*, that chain propagation occurs less readily in the $\text{ZnMe}_2\text{-O}_2$ reaction and the average chain length is less.

(4) *Di-n-propylzinc.*—This reaction has not been studied in great detail. It was decided to ascertain (a) whether the reaction is slow (as with the dimethyl compound), or fast (as with the diethyl), and (b) whether it is predominantly homogeneous or heterogeneous. No detailed investigation of the nature of the products has been made.

Rate of reaction at low pressures. The p - t curves were very similar to curve OBC, Fig. 1, and show that the reaction is of the fast type. At the reversal point the pressure of oxygen added was approximately half the original pressure of the dialkyl, suggesting that the rapid reaction is similar to that occurring with diethylzinc, *i.e.*,



The p - t curves did not reach their final slope for some time after the reversal point. This may be due to a further slow oxidation, *e.g.*, formation of ZnPr_2O_2 from ZnPr_2O . In one run, in which 1.84 mm. of dipropylzinc was used, the oxygen was stopped at the reversal point, and the vessel exhausted. On admitting 0.34 mm. of oxygen a slow contraction occurred—ca. 0.01 mm./min. This rate was doubled when the oxygen pressure was increased to 4 mm. It is therefore probable that if dipropylzinc were admitted to excess oxygen, oxidation to the second stage would occur, as with diethylzinc, but the low vapour pressure of the dipropyl compound complicates experimental verification of this.

During the rapid oxidation a liquid collected on the inlet tube. This had a very low vapour pressure, as it was not removed by 5 minutes' evacuation. During the second stage of the oxidation the substance appeared partly to solidify.

The total contraction at the reversal point was always rather less than would be expected from (4), assuming the product to have negligible vapour pressure. The discrepancy may be due to (1) ZnPr_2O having a small but not negligible vapour pressure, and/or (2) the formation of hydrocarbons, as was found with the other alkyls.

Tyndall beam. On admitting oxygen at a rate of 0.053 mm./min. to 1.93 mm. of dipropylzinc, the beam could be observed almost at once, being concentrated initially near the oxygen inlet. The beam rapidly expanded to fill the whole vessel, and disappeared after about one minute. On stopping the oxygen for two minutes and then restarting it, a similar result was obtained, the beam vanishing rather more rapidly.

In the second run, oxygen was admitted to a mixture of 1.10 mm. of dipropylzinc and 9.6 mm. of nitrogen. The beam was concentrated near the oxygen inlet for the first 6 minutes. At the end of this time it gradually spread throughout the vessel, and disappeared exactly at the reversal point.

These results are similar to those obtained with dimethylzinc and show that a homogeneous reaction occurs during the oxidation of dipropylzinc.

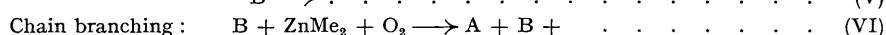
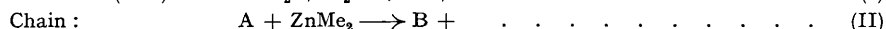
DISCUSSION.

Only in the case of dimethylzinc is the rate of oxidation slow enough to allow measurement. The main facts which have been established by the present experiments are as follows: (i) At low pressures, under suitable conditions, the Tyndall beam may be observed. Hence at least part of the reaction is homogeneous. (ii) The main product of oxidation is ZnMe_2O , even in the presence of excess of oxygen. (iii) In clean reaction vessels at low pressures the rate of reaction is proportional to $[\text{ZnMe}_2]^2$ and is independent of $[\text{O}_2]$ (except when the latter is very small). (iv) The solid products of oxidation catalyse the reaction: in dirty vessels the rate is proportional to $[\text{ZnMe}_2]$ and independent of $[\text{O}_2]$. (v) Inert gases have little or no effect on the rate of the reaction at low pressures. (vi) At higher pressures, as the ignition boundary is approached, the rate of reaction decreases with increase in oxygen pressure. (vii) Inert gases tend to decrease the rate of reaction near the ignition limit.

The fact that at low pressures the reaction is of zero order with respect to oxygen suggests very strongly that some surface process is involved. This is in agreement with the marked acceleration which occurs when the surface is coated with reaction products. Since there is undoubtedly a gas-phase reaction occurring, it seems likely that the oxidation is a chain process starting on the walls. In order to account for the observation that inert gases have no effect on the rate in the low-pressure experiments it must be further assumed that the chains also end on the walls. The observation by Thompson and Kelland (*loc. cit.*) that the rate of the "measurable" reaction is independent of vessel diameter is in agreement with this.

Turning to the runs at higher pressures, we may discuss the shape of the curves in Fig. 4. The initial lag and subsequent acceleration shown in Curves 1 and 3 may be accounted for in two ways. First, by analogy with the low-pressure experiments, the accumulation of solid product would be expected to lead to a gradual autocatalytic acceleration. Secondly, the curves are typical of branched-chain reactions, the rate increasing as the number of chains steadily builds up. Since the rate in these experiments increases with pressure of oxygen, the latter effect may be operative, with a branching reaction involving oxygen in a suitable manner. Curves 2 and 4, Fig. 4, show that with the pressures used in these experiments branching is less marked.

A general reaction scheme for the oxidation of dimethylzinc at low pressures is as follows, A and B being the chain carriers.



Since ZnMe_2O_2 is not the final product, a further reaction must be assumed :



If it is assumed that (VII) is fast compared to the other reactions, then the rate of reaction given by the above scheme [neglecting the consumption of ZnMe_2 in (I) and (VI)] is

$$-\frac{d[\text{ZnMe}_2]}{dt} = k_1 k_2 [\text{ZnMe}_2] f\{[\text{ZnMe}_2], [\text{O}_2]\} \times \frac{2k_3[\text{O}_2] + k_5}{k_4 k_5 + k_3 k_4 [\text{O}_2] + k_2 k_6 [\text{ZnMe}_2] - k_2 k_6 [\text{ZnMe}_2]^2 [\text{O}_2]} \dots \dots \text{ (5)}$$

where $k_1 f\{[\text{ZnMe}_2], [\text{O}_2]\}$ is the rate at which A centres enter the gas phase, from (I). It will be shown below that the experimental observations at low pressures with a dirty vessel are accounted for if $k_5 = 0$, and $f = \text{constant}$. This latter assumption is reasonable, as many surface reactions are of zero order. In clean vessels, it must be assumed that $f = [\text{ZnMe}_2]$. These assumptions regarding f are equivalent to assuming that the film of products adsorbs the alkyl and oxygen strongly, and becomes saturated at low pressures.

Putting $k_5 = 0$ in (5), we obtain the equation

$$-\frac{d[\text{ZnMe}_2]}{dt} = 2k_1 k_2 [\text{ZnMe}_2] f\{[\text{ZnMe}_2], [\text{O}_2]\} \times \frac{1}{k_4 - k_2 k_6 [\text{ZnMe}_2]^2 / k_3} \dots \dots \dots \text{ (6)}$$

Both k_1 and k_4 will depend on the total gas pressure : they may be assumed to be inversely proportional to the total pressure (X). Further, when branching is important the rate will depend on the vessel diameter (d). This introduces a factor d^2 into the branching term in (6) (see, *e.g.*, Lewis and Van Elbe, "Combustion, Flames & Explosions of Gases," Camb. Univ. Press, 1938, Ch. I). Thus (6) becomes :—

$$-\frac{d[\text{ZnMe}_2]}{dt} = 2k_1' k_2 [\text{ZnMe}_2] f\{[\text{ZnMe}_2], [\text{O}_2]\} \times \frac{1}{X \left(\frac{k_4'}{X} - \frac{k_2 k_6}{k_3} [\text{ZnMe}_2]^2 d^2 \right)} \dots \dots \dots \text{ (7)}$$

where k_1' , k_4' , and k_6' are constants.

At low pressures of reactants the branching reaction (VI) will be negligible. Under these conditions, if we make the above assumptions about f , (7) predicts rates which are independent of $[\text{O}_2]$ and the total pressure and are proportional to $[\text{ZnMe}_2]^2$ and $[\text{ZnMe}_2]$ in clean and in dirty vessels respectively. This is in agreement with observation.

In the high-pressure runs represented by curves 1 and 3 of Fig. 4, $X \sim \{[\text{O}_2] + [\text{ZnMe}_2]\}$ and (VI) is no longer negligible. The reaction velocity should thus increase with increase in $[\text{O}_2]$, as found experimentally. When inert gas, *e.g.*, nitrogen, is present, $X \sim \{[\text{O}_2] + [\text{N}_2] + [\text{ZnMe}_2]\}$. Thus the velocity should increase with increase in $[\text{N}_2]$. In practice, however, inert gas causes a small decrease in velocity. This indicates that the inert gas is suppressing the branching reaction. It may do this, for example, by partial deactivation of B, which while leaving (III) unaffected may suppress (VI).

Qualitatively therefore (7) is in satisfactory agreement with experiment. Equation (8), which is of the same form as (7) with $f = [\text{ZnMe}_2]$ and $X = \{[\text{ZnMe}_2] + [\text{O}_2]\}$, gives reaction rates which are reasonably close to the observed one in clean vessels over the whole pressure range (rate in mm./sec.; concentrations in mm.). The experimental and calculated values are compared in Tables IV and V.

$$\text{Rate of contraction} = -\frac{d[\text{ZnMe}_2]}{dt} / 0.74 = \frac{[\text{ZnMe}_2]^2}{1000 - 1.78 \times 10^{-2} d^2 \{[\text{ZnMe}_2] + [\text{O}_2]\} [\text{ZnMe}_2]^2} \dots \dots \text{ (8)}$$

According to (7) a chain isothermal explosion should occur when

$$\frac{k_2 k_6'}{k_3} [\text{ZnMe}_2]^2 \{ [\text{ZnMe}_2] + [\text{O}_2] \} d^2 = k_4' \quad \dots \quad (9)$$

Thompson and Kelland (*loc. cit.*) reported that in a cylindrical vessel ($d = 4.5$ cm.), $[\text{ZnMe}_2]^2[\text{O}_2]$ was constant at the ignition boundary. This was not so in a narrower vessel ($d = 2.5$ cm.). In this case $[\text{ZnMe}_2]^2\{[\text{ZnMe}_2] + [\text{O}_2]\}$ is more nearly constant than the simpler expressions, although not satisfactorily so.

Presumably the ignition region is bounded by a closed curve, which is determined by reaction (IV), and chain-breaking reactions at higher pressures not shown in the above scheme. Thompson and Kelland located a portion of this boundary, but the lay-out of the remainder is unknown, and would probably be difficult to determine for practical reasons. In the absence of this information, and without knowledge of the variation of reaction rate over wider ranges of pressure of reactants than is now available, it is not fruitful to discuss the conditions for ignition much further. It may be noted, however, that (8) and (9) predict explosion at pressures rather lower than found experimentally. Thus with $[\text{O}_2] = 45$ mm. ($d = 6$ cm.), the calculated limiting pressure of ZnMe_2 is 5.5 mm., whereas the experimental value is 8.4 mm. This may imply that some chain breaking by oxygen is going on even at these pressures. However, even in this region of pressures, the practical difficulties are considerable. During the lag before explosion a reaction occurs, so that the initial pressures are appreciably higher than those at the moment of explosion. Further, near the boundary, the time of addition of oxygen is sufficiently large to cause uncertainty. If it is assumed that chain breaking by oxygen is not important at 45 mm. pressure, the above considerations seem to indicate that ignition is ultimately an isothermal chain process. This is in agreement with Thompson and Kelland's observation that the oxidation process has a very small temperature coefficient.

There are a number of possible alternatives for the chain carriers, *e.g.*, (i) $A = \text{O}$, $B = \text{ZnMe}_2\text{O}$, the latter being an excited molecule or radical. This scheme is possible energetically (unpublished values for the heat of combustion of ZnMe_2 obtained by Dr. L. H. Long). (ii) $A = \text{ZnMe}_2\text{O}_2^*$, $B = \text{ZnMe}_2^*$, giving a thermal chain. This mechanism would need the assumption that, while collisions between inert gas molecules and the active centres do not prevent the latter participating in (II) and (III), they deactivate B sufficiently to impede (VI).

Similar reactions may occur during the oxidation of diethyl- and dipropyl-zinc, except that the chain-propagating processes are much faster, relative to (VII). When diethylzinc is added slowly to excess of oxygen, the chain reaction is so rapid that $[\text{ZnEt}_2]$ is kept extremely low, and (VII) cannot occur to an appreciable extent. Thus the main product is ZnEt_2O_2 . On the other hand, when oxygen is added to diethylzinc, (VII) is important, and ZnEt_2O is formed. In other words, with dimethylzinc, (VII) is rapid compared to the chain-propagating reaction, while with diethylzinc all three reactions are about equally fast.

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