186. *The Oxidation of Dimethylzinc.*

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Kinetic measurements upon the oxidation of hydrocarbons and certain of their simpler derivatives have been made in recent years with a view to determining the mechanism of these processes. It has in general been found that the idea of reaction chains suffices to explain the observed phenomena, and a formal understanding of the reactions has been arrived at. Many of the details involved are not, however, clear. Of these, probably the most significant is the knowledge of the precise intermediate products and " elementary processes " in the reactions. Several investigators suggest the production of free alkyl radicals, which are subsequently oxidised, but in all cases the mechanisms proposed are mainly hypothetical. It therefore seemed desirable to examine if possible the oxidation of free alkyl radicals in separate experiments.

Few measurements of this kind have so far been made. There are obvious difficulties involved, *e.g.*, the lack of certainty of the production of the free radicals and their short life when produced (Paneth and Hofeditz, *Ber.*, 1929, **62**, 1335; Paneth and Lautsch, *Nature*, 1930, **125**, 564; see also Meinert, *J. Amer. Chem. Soc.*, 1933, **55**, 979; Simons, McNamee, and Hurd, *J. Physical Chem.*, 1932, **36**, 939; Geddes and Mack, *J. Amer. Chem. Soc.*, 1930, **52**, 4372; Taylor and Jones, *ibid.*, p. 1111). The most relevant work is that of Bates and Spence (*ibid.*, 1931, **53**, 1689), who studied the photochemical oxidation of methyl iodide. The absorption spectrum of methyl iodide vapour, together with quantum-efficiency experiments, indicated that the primary act in the absorption of the radiation by the methyl iodide is one of splitting into the methyl radical and an iodine atom. Subsequent oxidation of the methyl radical occurs.

It seemed probable that measurements on the oxidation of the vapours of alkyl derivatives of certain elements would be helpful, and dimethyl- and diethyl-zinc, tetraethyl-lead, triethylphosphine, and trialkylamines were chosen. These measurements have additional interest in two directions. First, it is well known that tetraethyl-lead and similar substances may be used as anti-knocks in the combustion of hydrocarbons, although their exact function is not known. Secondly, it is remarkable that dimethylzinc and diethylzinc ignite spontaneously in air or oxygen at ordinary temperatures. In the oxidation of phosphine, again, explosion-limit phenomena have been discovered of a type sometimes noticed in chain reactions. It was thought interesting to ascertain whether triethylphosphine, which is spontaneously oxidised, also exhibits such behaviour, for in this case it might be possible to correlate the various sets of phenomena.

The experiments to be described relate to the oxidation of dimethylzinc vapour. No kinetic measurements on this process have previously been made. The products of the action of oxygen on dimethyl- and diethyl-zinc, usually in solvents, have been examined by Frankland, Butlerow, and Meyer individually. Frankland (*Annalen*, 1853, **85**, 347) found that dimethylzinc " inflames " in air with the production of white fumes, while in pure oxygen " explosion " occurs; the products of the slow reaction were long in doubt, and those of the explosion are not reported. Frankland first thought that the white fumes consisted of zinc oxide, but later work on the oxidation of diethylzinc in ethereal solution led him to propose the formation of an alkoxide, $Zn(OCH_3)_2$.

On the other hand, Butlerow (*Z. Pharm. Chem.*, 1864, **7**, 402) argued for the formation of a methoxy-methyl derivative in the oxidation of dimethylzinc in methyl iodide solution, the latter being used, like Frankland's ether, to prevent the explosive oxidation; the white crystalline product, on hydrolysis by water, liberated one equivalent each of methyl alcohol and methane, and on analysis proved to be largely methylzinc methoxide, $ZnMe{\cdot}OMe$, mixed with a little zinc methoxide, $Zn(OMe)_2$. In confirmation of this view, he showed that the product of the interaction of one equivalent of dimethylzinc with one of methyl alcohol was identical with that of the slow oxidation of dimethylzinc, although excess of methyl alcohol yielded a new product which, on hydrolysis with dilute sulphuric acid, yielded two equivalents of alcohol and was hence the dimethoxy-derivative. The same arguments applied to the oxidation of diethylzinc.

In view of this evidence Frankland suggested that, in the oxidation in ethereal solution, methylzinc methoxide is first formed as a cloud, but dissolves in the ether, and on further oxidation the dimethoxy-derivative separates. He supposed that in Butlerow's experiments the former compound separated owing to its insolubility in methyl iodide.

The question was reopened in 1890 by Meyer (*Ber.*, **23**, 396) when he oxidised diethylzinc in ligroin, and obtained a product which he regarded as a type of peroxide since it liberated iodine from potassium iodide. On hydrolysis with acid it gave ethyl alcohol and no hydrocarbon, and it was further quite different from the product of the reaction between diethylzinc and ethyl alcohol. Meyer also observed that this oxidation product decomposed explosively on heating and assigned to it the structure $ZnEt{\cdot}O{\cdot}OEt$. Hydrolysis to ethyl alcohol could then be explained in the following manner :

$$\underset{\mathrm{HO}}{\mathrm{C_2H_5}{\cdot}}\,\vdots\,\mathrm{Zn{\cdot}O{\cdot}}\,\vdots\,\underset{\mathrm{H}}{\mathrm{OC_2H_5}} \longrightarrow 2\mathrm{C_2H_5{\cdot}OH} + \mathrm{ZnO}.$$

For the reaction in the gas phase it now appears possible to reconcile the various observations. Dimethylzinc under certain conditions of pressure undergoes a slow oxidation in which methylzinc methoxide is the final product, but the peroxidic compound $ZnMe_2O_2$ or $ZnMe{\cdot}O{\cdot}OMe$ or $Zn(OMe)_2$ may be an intermediate stage. Preliminary experiments on the oxidation of diethylzinc (following paper) show that the more fully oxygenated compound $ZnEt_2O_2$ is probably the final product. In the explosive oxidation of dimethylzinc, decomposition of the oxygenated compounds occurs, giving gaseous products and zinc oxide, with some zinc or carbon.

EXPERIMENTAL.

The reaction was followed by the static method usually employed where a change in pressure accompanies the reaction. The reaction vessel was suspended in a water-bath, the temp. of which could be varied. Later expts. showed that a more careful control of temp. was unnecessary since the reaction velocity is hardly affected by changes in temp. Dead space was minimised by using capillary connecting tubes, and pressure changes were recorded on a Hg manometer. Since the press. changes involved were rather small, this procedure might be criticised, but it was the most convenient available, and experience showed that trustworthy results could be obtained. Attempts to use a H_2SO_4 manometer failed both because the acid reacted with the $ZnMe_2$ and because the time of lag of the viscous liquid was too great. The reaction vessel was connected to storage vessels containing $ZnMe_2$, O_2, and inert gas respectively, to a pump, and to a pipette into which gas samples could be drawn. The apparatus was evacuated by means of a Hg-vapour pump backed by a H_2O pump, and finally by a vacuum bottle.

The $ZnMe_2$ was supplied (Harrington) in sealed tubes, which were cracked by shaking in the evacuated storage vessel; the first fractions were somewhat impure, but after removal of these, reproducible results were obtained. O_2, N_2, and A were taken from cylinders and dried by P_2O_5. CO_2 was prepared by heating $MgCO_3$, and Me_2O which was used in certain expts. was obtained by the general method from MeOH and conc. H_2SO_4. MeI (Harrington) was used as supplied pure.

$ZnMe_2$ was added first to the reaction vessel, then inert gas, if required, and finally O_2 as rapidly as possible, since the reaction is very rapid. The start of the reaction was taken as the moment of complete addition of the O_2. Reversal of the order of addition of the gases did not appreciably alter the results, but since, as shown later, the rate is more dependent upon the concn. of $ZnMe_2$ than on that of O_2, it was desirable to add the former first and measure its press. accurately.

Apiezon tap grease was employed; it was not rapidly attacked by the $ZnMe_2$ vapour and no great inconvenience was caused in this respect (contrast $ZnEt_2$, succeeding paper).

Results.

The expts. to be described indicate that at low press. and room temp. it is possible to measure a very rapid reaction between $ZnMe_2$ vapour and O_2. With higher pressures of either reactant explosion occurs. The products of the slow reaction are solid at the temps. employed, but in the ignition, gaseous products are obtained, consisting mainly of CO, CH_4, and H; a solid product is also formed in the explosion. The solid formed in the slow reaction is amorphous and white, whereas that deposited in the ignition is darker; the former consists primarily of

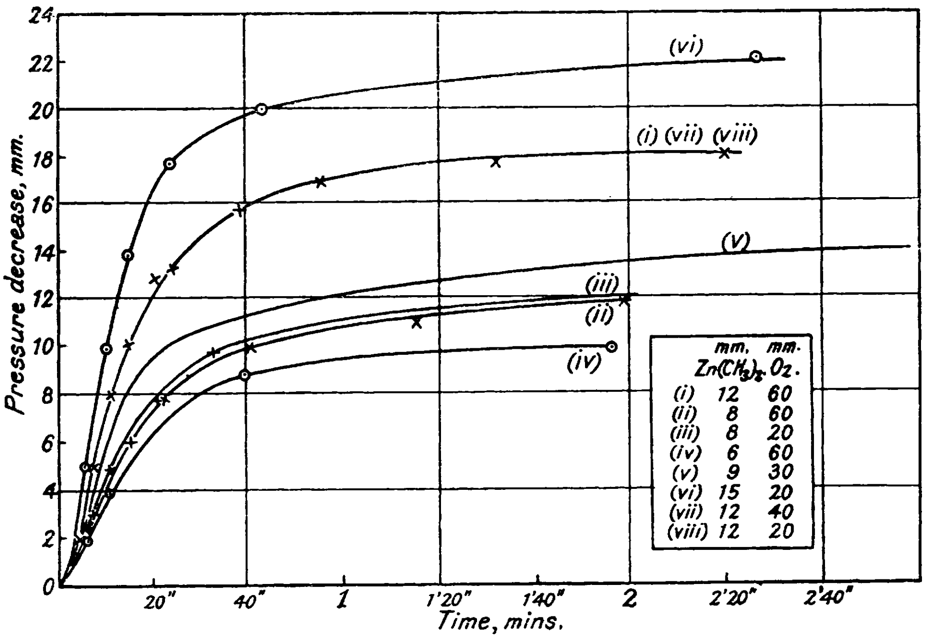
ZnMe·OMe, and the latter of Zn and ZnO. The influence of various factors, *e.g.*, initial press., temp., vessel dimensions, and the addition of inert gases, upon the velocity of the slow reaction has been investigated. The manner in which this slow reaction passes into explosion, and the influence of similar factors upon the highest pressures employable for the maintenance of a slow reaction have also been studied.

The Measurable Reaction.—In the measurable reaction a decrease of press. is observed which is always approx. 150% of the initial press. of $ZnMe_2$, provided that the initial press. of O_2 exceed one-half that of the $ZnMe_2$; if this condition is not fulfilled, the decrease in press. is three times the initial press. of O_2 :

Initl. press., mm. $ZnMe_2$	12	8	8	6	12	15	9	22	19	15	17
O_2	60	60	20	60	40	20	30	12	10	5	5·5
Press. decrease, mm.	18	11·5	12	9·5	17·5	22·5	14	34	28	15	17·5

The gases remaining were analysed. It is significant that CO, CO_2, CH_4, C_2H_4, and H were not present in appreciable quantity. Tests for CH_2O by Schryver's reaction (cf. Thorpe and Whiteley, " Organic Analysis," p. 99) gave negative results. Aldehydes and methylal were shown to be absent by means of resorcinol and conc. H_2SO_4 (*op. cit.*, p. 100). In those expts. in which the initial press. of O_2 exceeded half the press. of $ZnMe_2$ the only gas remaining was O_2, and with initial mixtures $2ZnMe_2 + 1O_2$ the press. fell to almost zero.

FIG. 1.



The white amorphous solid product of the measurable reaction reacted vigorously with H_2O, evolving CH_4. Of the possible explanations of these facts, only two are probable. (1) It is conceivable that Me_2O is first produced, co-ordinating itself rapidly with a second mol. of $ZnMe_2$: $ZnMe_2 + O_2 \longrightarrow ZnO + Me_2O$; $Me_2O + ZnMe_2 \longrightarrow ZnMe_2,Me_2O$, as in the co-ordination of Et_2O with Grignard reagents. Moreover, Frankland found that Et_2S is formed in the reaction of S with $ZnEt_2$.

(2) ZnMe·OMe is formed, but, unless it is assumed that the O_2 mol. is dissociated in some way into atoms, the production of this substance in one stage would necessitate the ternary collision $2ZnMe_2 + O_2 \longrightarrow 2ZnMe{\cdot}OMe$; it seems more probable, therefore, that this compound would be formed in two stages : $ZnMe_2 + O_2 \longrightarrow ZnMe_2{:}O_2$; $ZnMe_2{:}O_2 + ZnMe_2 \longrightarrow 2ZnMe{\cdot}OMe$.

The first alternative has been tested by allowing $ZnMe_2$ vapour to remain in contact with Me_2O at the appropriate temps. No interaction could be observed over long periods, even when using pressures much higher than would be involved in the particular case. The second alternative is therefore favoured, and agrees with the earlier results already outlined. Several structures are possible for the addition compound of the $ZnMe_2$ with O_2: it may be either the dimethoxide, or a substance of peroxidic character and formula ZnMe·O·OMe, or $O_2 \rightarrow ZnMe_2$. Compounds of the latter type can definitely be isolated. The kinetic experiments given below appear to substantiate the idea of the primary peroxide formation.

" Order " and course of the reaction. The curves shown in Fig. 1 exhibit the course of the measurable reaction for a series of different initial reactant concns. (see Table I). Measurement of the initial rates in such expts. shows that the " order " is approx. unity with respect to $ZnMe_2$ and zero with respect to O_2. It is important, however, to note that a slight induction period precedes the reaction. This might be due to autocatalysis, in which case measurement of the initial rate would be difficult; its significance is discussed below. The values given for the order ignore the induction period, the " start " being taken as the instant when press. decrease is first observed.

TABLE I.

Initl. press., mm.		Initial rate,			
$ZnMe_2$.	O_2.	mm./sec.	*x*.		*y*.
8	20	0·6	0·0	0·0	—
8	30	0·65			
8	60	0·55	0·1		
6	20	0·38	0·0		—
6	60	0·40			

Initl. press., mm.		Initial rate,			
$ZnMe_2$.	O_2.	mm./sec.	*x*.		*y*.
12	20	0·83	−0·1	0·0	—
12	40	0·72			
12	60	0·82	0·1		
6	20	0·38	—		1·0
12	20	0·83			
6	60	0·40	—		1·0
12	60	0·83			

x = order with respect to oxygen, y = order with respect to dimethylzinc.

The direct proportionality between rate and $ZnMe_2$ concn. is better shown in the following table, which gives values for the proportionality const., $k = [ZnMe_2]/\text{rate}$.

$ZnMe_2$ concn.	20	15	14	12	10	9	8	6
Initial rate	1·45	1·00	0·91	0·80	0·67	0·62	0·54	0·40
k	13·8	15·0	15·4	15·0	15·0	14·5	15·4	15·0

That the period of half change in the reaction is approx. const. when different initial concns. are used is further confirmation of the result that the total order of the reaction is nearly unity.

The induction period is decreased, and the velocity slightly increased, as the clean reaction vessel becomes coated with deposit; the first runs in a clean vessel are rather slow, and in these circumstances the total order of reaction is usually rather higher than unity, approaching a value of two.

With some samples of $ZnMe_2$ the first fractions appeared extremely unreactive, but the inertness disappeared after some of the liquid had been distilled off. It was at first thought that traces of MeI were responsible for the anomaly, since this substance may well remain in the $ZnMe_2$ after its prepn. The addition of MeI vapour in subsequent expts. proved, however, that this was not so; in fact, this substance behaves as an inert gas. This phenomenon still awaits explanation.

Influence of temperature. Measurements were made at several temps. over the range 0—40° and also at 100°. The velocity of the measurable reaction is hardly at all dependent upon temp. and the end-point is unaffected. Over the range 0—40° there is no noticeable change; at 100° the rate is somewhat greater, but probably is not more than three times that at 0°. It is therefore evident that some process is occurring with very small energy of activation.

Influence of vessel dimensions. The velocity of the measurable reaction for given initial concns. was compared in two cylindrical vessels 4·5 and 2·5 cm. in diam. The difference was not marked. In a vessel packed with glass wool the rate was increased 3- or 4-fold.

Addition of inert gases. In the presence of A and CO_2, the reaction velocity is not noticeably affected and the end-point remains the same (see Fig. 2).

The Explosive Reaction.—If the pressures of $ZnMe_2$ and O_2 exceed certain values, the measurable reaction gives way to an explosive oxidation, preceded, as before, by an induction period. With higher pressures of O_2, there is an increase in press. in the explosion, accompanied by a flash and the production of a black solid, but with lower O_2 concn. a decrease in press. without flash is observed, sometimes corresponding to that decrease which would be obtained in the measurable reaction; when such a decrease in press. occurs the deposit is white. The two processes are essentially different (see p. 753), the latter being an oxidation, as in the measurable reaction, and the former an explosive decomposition.

The gaseous products of the instantaneous reaction were analysed. It is remarkable that CO_2 is hardly ever found in appreciable quantity; qualitative tests with baryta indicated that it was formed in those cases only in which a high proportion of O_2 was used. Qualitative tests for formaldehyde (Schryver's reaction) and for acetaldehyde proved negative. The principal products are CO, CH_4, and H_2; C_2H_4 was occasionally found in small quantity. The ratio CO/CH_4 increased with increase in the ratio $O_2/ZnMe_2$. The results are shown in Table II. CO_2 was absorbed by KOH, O_2 by alk. pyrogallol, C_2H_4 by Br aq., CO by ammoniacal CuCl, and CH_4 and H_2 were determined by combustion.

The investigation of this " explosion " phenomenon centres on the determination of the limiting pressures required to bring it about, and the way in which these pressures are affected by a variety of circumstances. In general, for any initial concn. of $ZnMe_2$, there exists a limiting O_2 press. and *vice versa*; although with $ZnMe_2$ concns. below a certain value no increase of O_2 press. is sufficient to bring about explosion.

FIG. 2.

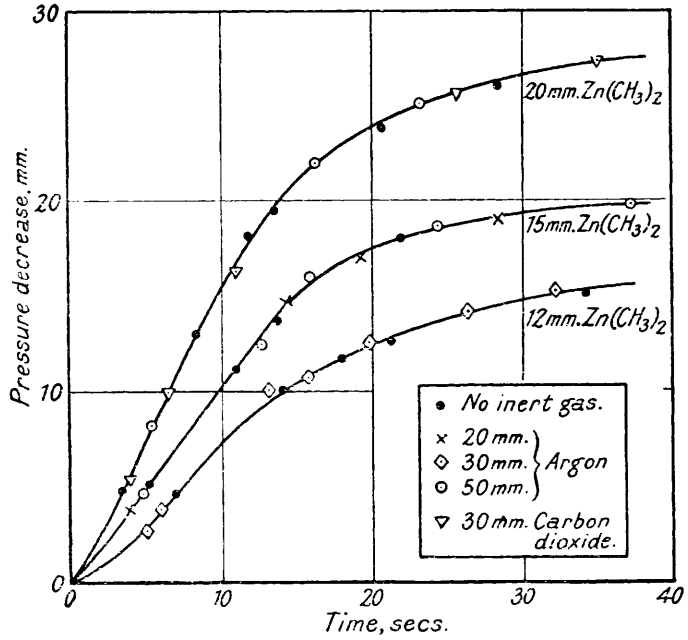


TABLE II.

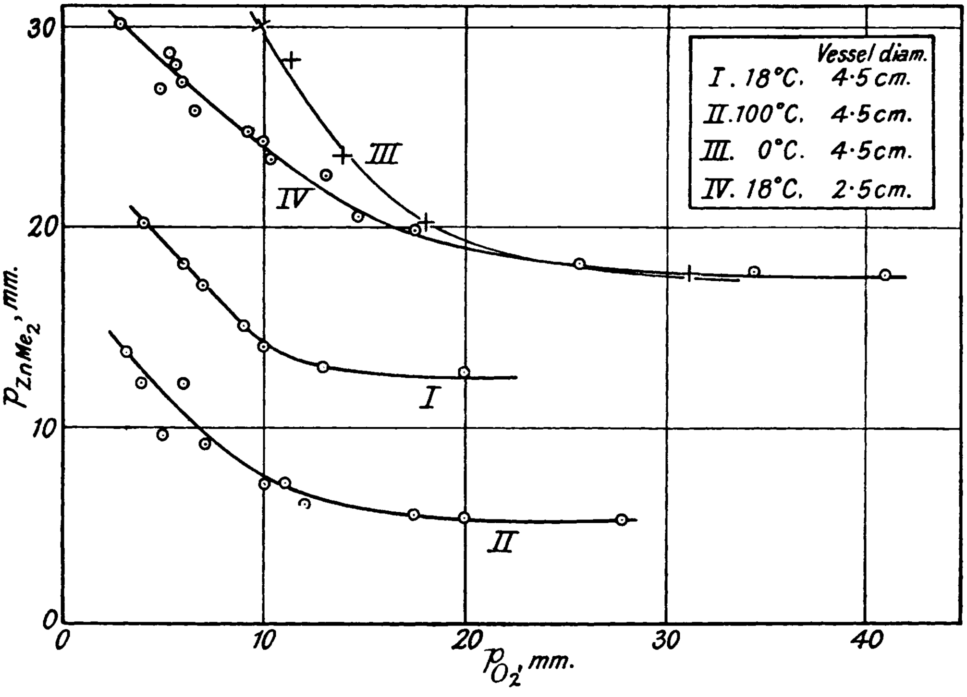
Press., mm.			Gaseous products, %.						
$ZnMe_2$.	O_2.	Ratio.	CO_2.	O_2.	CO.	C_2H_4.	CH_4.	H_2.	Total.†
22	40	0·55	0·7	10·0	30·4	1·6	18·6	35·3	96·6
24	26	0·9	0·9	2·6	34·3	0·0	19·0	41·2	98·0
23	24	0·95	1·8	2·7	35·3	1·1	15·6	40·0	96·5
25	25	1·0	1·95	2·7	33·6	0·3	17·6	40·9	97·0
19	16	1·2	1·4	4·1	32·9	0·0	14·1	44·7	97·2
21	14	1·5	1·1	3·7	30·6	1·9	17·1	44·0	98·4
29	18	1·6	3·4	2·9	22·4	6·4	31·6	32·2	98·9
28	17	1·6	2·0	5·1	15·0	8·5	43·2	24·2	98·0
26	16	1·6	1·9	3·8	23·6	6·3	32·4	29·9	97·9
20	10	2·0	2·6	5·2	15·6		not analysed		
19	8	2·4*	2·0	3·5	25·85	1·65	24·0	40·0	97·0

* With very low proportions of O_2, the gases were difficult to analyse owing to the small amounts available.

† The failure to total 100% is due to the fact that the combustion data do not exactly tally. The contraction in the combustion is always rather less than would be expected on the basis of the given composition (in terms of CH_4 and H_2). This seems not to be due to error but rather to some other products, *e.g.*, other hydrocarbons, which mask the analyses.

Fig. 3 exhibits (*a*) the relationship between the press. of $ZnMe_2$ and O_2 in a vessel 4·5 cm. in diam. at three temps., and (*b*) the same relationship in two different vessels at the same temp. It is clear from Fig. 3 that increase in temp. diminishes the limiting pressures for the explosion. The quant. significance of this is discussed below.

FIG. 3.



For the purpose of constructing some mechanism for the process, it was interesting to discover the precise relationship between the press. of $ZnMe_2$ and of O_2 in a given vessel at a given temp. The data are summarised in Table III.

TABLE III.

p_1 = Pressure of $ZnMe_2$, mm.; p_2 = pressure of O_2.

A. Larger reaction vessel; 4·5 cm. internal diameter.

p_1.	p_2.	p_1p_2.	$p_1^2p_2$.	$p_1 + p_2$.	p_1.	p_2.	p_1p_2.	$p_1^2p_2$.	$p_1 + p_2$.
Temp. 0°.									
30	10	300	9000	40	20	18	360	7200	38
28	11	308	8626	39	18·5	20	370	6845	38·5
23	14	322	7405	37	18	27	486	8750	45
Temp. 19°.									
20	4	80	1600	24	15	9	135	2025	24
18	6	108	1944	24	14	10	140	1960	24
17	7	119	2023	24	13	13	169	2197	26
Temp. 100°.									
12	4·5	54	720	16·5	7	10	70	490	17
10	6	60	600	16	6·5	11·5	74·5	486	18
9	7	63	637	16	5·5	17·5	96	529	23
B. Smaller reaction vessel; 2·4 cm. internal diameter; temp. 19°.									
30	3	90	2700	33	24	10·5	252	6048	34·5
27	5	135	3645	32	21	15	315	6615	36
26	7	182	4732	33	19	20	380	7220	39
25	9	225	5634	34	17	40	680	11560	57

It is clear that although p_1p_2 is not const. in a given vessel at any temp., yet $p_1^2p_2$ is fairly so except in the narrower vessel. The remarkable fact is that the sum of the partial pressures of $ZnMe_2$ and O_2 is const. at any temp. in a given vessel.

The addition of CO_2 affects the limiting pressures of $ZnMe_2$ and O_2 for the explosion. With a given press. of $ZnMe_2$ the lowest press. of O_2 for explosion is in general raised in the presence of inert gas. The curves exhibiting this relationship (Figs. 4 and 5) show that the effect is not uniform; at relatively low pressures of inert gas the O_2 limit is not much affected, but at a certain concn. of inert gas there is a rather sudden increase in this limit.

FIG. 4.

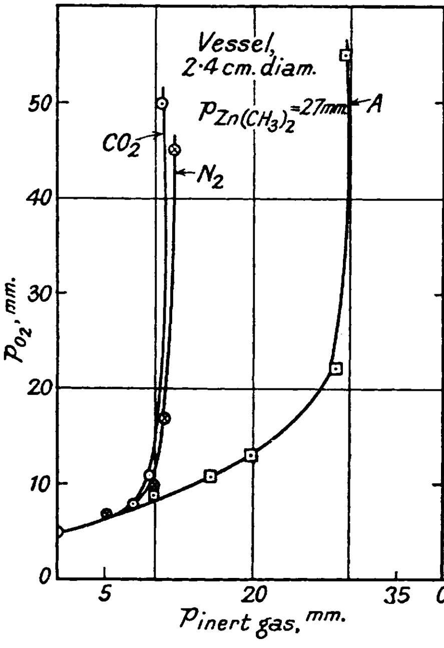
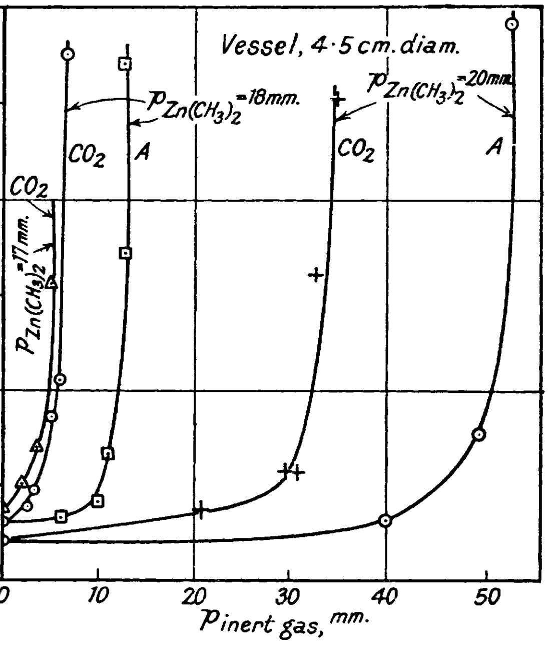


FIG. 5.



DISCUSSION.

The processes involved in the reaction between dimethylzinc vapour and oxygen are very complicated. Although the following discussion affords a reasonable explanation of their general nature, it can only be regarded as preliminary pending further work. It is hoped that the systematic examination of the oxidation of the vapours of the series of metal and non-metal alkyls indicated on p. 746 will provide data for a more precise theory, which will disclose their individual similarities and differences.

It is first important to notice that in the oxidation of dimethylzinc vapour under the conditions described above, the process consists, not in oxidation of alkyl groups, but in oxidation of the molecule as a whole, and in the "explosion," a decomposition of the oxygenated product takes place, the products being carbon monoxide, methane, hydrogen, and zinc oxide. Aldehydes or carbon dioxide are not found in appreciable quantity.

There are many peculiar features of the process. Perhaps the most striking is the extreme rapidity of the measurable oxidation. At all pressures, from those giving rise to instantaneous reaction down to the smallest which could be conveniently measured, the process was completed within *ca.* 2 minutes, the period of half change being as short as 20 seconds. At the very small pressures involved, this corresponds to a very rapid process indeed. Attempts to retard the reaction by decrease of either pressure or temperature are frustrated—on the one hand, because a satisfactory measurement of the extremely low and rapidly changing pressures has not yet been devised (although one is now being considered), and on the other, because the vapour pressure of dimethylzinc rapidly decreases below 0°; our measurements indicate, however, that in the vicinity of 0°, at least, the rate is not much affected by temperature. Since the reaction velocity is approximately trebled over the range 0—100°, the energy of activation must be very low—of the order 3000 cals. The process is, however, probably highly exothermic.

Characteristics of this kind suggest a similarity of the process to those involved in the so-called highly diluted flames of Polanyi and his co-workers (Polanyi, " Atomic Reactions," London, 1932; Schay, " Hochverdünnte Flammen," *Fortschr. Chem. Physik*, 1930, **21**, 1). It might be argued that the measurable interaction of dimethylzinc and oxygen is a " slow " flame, and it is possible that further examination will reveal some connexion between the individual groups of phenomena. Nevertheless, the reaction under consideration seems a quite definite and measurable process : the curves exhibiting its course are precise and of the usual type, and the end-points are reproducible.

Moreover, if the measurable process were simply a " slow " flame, it would be expected that increase in concentration of the reactants should accelerate the process uniformly up to the point of explosion. Whilst the oxygen concentration has no noticeable effect upon the reaction velocity, increase in that of dimethylzinc usually leads to increased rate, culminating in instantaneous reaction. At the same time it is possible under certain conditions (not entirely controllable) to convert a reaction rate which is by no means the highest amenable to measurement into instantaneous interaction by a very small pressure change of dimethylzinc. Thus the idea that with increasing concentrations of reactants the process gradually becomes non-isothermal is weakened.

Apart from this, however, there are important reasons for believing that the measurable change is in principle to be differentiated from the explosive one. For example, although oxygen concentration has no noticeable influence upon the measurable rate, yet in general it facilitates the explosion, in the sense that a decrease in the dimethylzinc concentration below the explosion limit can be compensated by an increase in that of oxygen (Fig. 3). Further, although increase of temperature does not appreciably affect the velocity, yet it reduces the explosion limits (Fig. 3). The influence of the dimensions of the reaction vessel is somewhat uncertain; although the rate of the measurable process is not much affected by packing, yet the explosion is completely stopped in a vessel packed with glass wool. Decrease in the vessel diameter also displaces the explosion limit curve, $p_{Zn(CH_3)_2}$ plotted against p_{O_2}, to higher values of pressure.

The function of added inert gas is perhaps the most striking. Argon and nitrogen have little influence upon the measurable interaction, but in the explosion they have a peculiar effect (see Figs. 4 and 5) : for a given concentration of dimethylzinc, the critical oxygen pressure is at first not much affected by increasing addition of inert gas, but eventually a point is reached when the critical oxygen pressure very suddenly rises to high values. There is here a kind of " limit " phenomenon. The high rate of reaction and the marked exothermic nature of the changes suggest the intervention of reaction chains; moreover, the final product, methylzinc methoxide, could only be produced in one stage by a ternary collision and at the pressures involved this is extremely unlikely.

The theory of reaction chains (cf. Hinshelwood, " Kinetics of Chemical Change," Chap. 6) provides a general expression for the rate of a reaction of the form

$$\text{rate} = f(c)/[f'(c) + f''(s) + A(1 - \alpha)]$$

where $f(c)$, $f'(c)$, $f''(s)$ are functions of the reactant concentrations (c) or of surface (s), A is a constant, and α a measure of the probability that a chain shall branch. α varies with the pressure of the reactants, and $f'(c)$ and $f''(s)$ involve processes of deactivation by gas or wall. So long as $\alpha \leqq 1$, the expression has a finite value, which can either be large or small according to the relative values of $f(c)$ and $f'(c) + f''(s)$. If $\alpha > 1$ there will be conditions such that the denominator of the above expression becomes zero and the rate infinite, *i.e.*, explosive. This change in α from $\leqq 1$ to > 1 might occur with a minute alteration in pressure and if $f'(c) + f''(s)$ were very small, the slight change in α necessary would mean that the transition to explosion should be abrupt. Formally, therefore, we should expect to find two types of reaction chain; examples of both types have been described (Hinshelwood, *op. cit.*). The important result is that in the examples so far studied the conditions of temperature and pressure required for abrupt discontinuity (limit phenomena) are not at all the same as those which give a conveniently rapid measurable reaction : there is either a fairly rapid but measurable change tending to " thermal " ignition at higher pressures, or a very low reaction velocity which can pass suddenly into explosion. Nevertheless, there is no reason why, if $f(c)$ is very large, a region of high but measurable reaction rate should not overlap one of " branching chain " explosion, and this seems to occur in the oxidation of dimethylzinc.

The details of the process have still to be explained. At first, the low order, independence of the rate of oxygen concentration, its very small temperature coefficient, and independence of added inert gases, suggested that the measurable reaction was a surface process. Against this supposition was the very slight effect of packing with glass-wool, and also the fact that the white nuclei of the product are first seen to form in the gas and then to separate slowly on to the walls of the vessel; moreover, the temperature coefficient is abnormally low.

If reaction chains are involved, packing would retard the process if the active centres were destroyed on the walls. That this does not occur implies that the principal deactivation is in the gas, and also that chains may be short. If by a suitable alteration in conditions, such as increase of dimethylzinc concentration above a certain value, α becomes greater than 1, then the chains may rapidly lengthen and the activation processes get out of hand as compared with those leading to chain stoppage. This will lead to inflammation.

The effect of added inert gases suggests that they bring about the removal of active centres in some way, and at the appropriate pressure can become so effective as to reduce α below unity and convert an unstable state into a stable one. The inert gas does not lower, but raises the critical pressure of oxygen for a given dimethylzinc concentration, and cannot therefore, primarily at any rate, function in such a way as to prevent a diffusion of active centres to the walls where they may be destroyed (cf. Melville and Ludlam, *Proc. Roy. Soc.*, 1931, **132**, *A*, 108; Thompson, Hovde, and Cairns, this vol., p. 208; Melville, *Trans. Faraday Soc.*, 1932, **28**, 814). (Surface deactivation plays an insignificant rôle in the measurable reaction where the chains are probably short, but with long chains it is more in evidence, and the vessel dimensions somewhat affect the limiting pressures.)

It seems unlikely, however, that the inert gases simply take away excess energy from active products and " cool " the mixture, for if this were so, argon should be slightly more effective than nitrogen or carbon dioxide, whereas the reverse is found. If nitrogen is effective by a physical process of any kind, oxygen also should possess this property to some degree : in the same way that nitrogen at a certain concentration suddenly inhibits the explosion, so we might expect oxygen to be effective, and there should be an " upper " limit in the $p_{Zn(CH_3)_2}$–p_{O_2} graph, *i.e.*, for any given pressure of dimethylzinc there should be both a lower and an upper limiting pressure of oxygen for explosion, higher pressures producing only a rapid reaction. The detection of this limit is difficult for experimental reasons, but the following experiment shows that it exists.

Dimethylzinc vapour was sealed in small thin-walled tubes (of known volume) at different known pressures. A tube filled in this way was introduced into a spherical glass globe, which was then evacuated, filled with oxygen to a measured pressure, and the tube broken by shaking. The volumes were so arranged that the pressure of the dimethylzinc after the breaking was approximately 20 mm.—well above the " minimum " pressure for explosion at 18°. On breaking there was no flash or sign of explosion if the pressure of oxygen exceeded about 600 mm., but the white solid product was rapidly formed.

The failure of inert gases to retard the measurable process is probably to be explained by the fact that the chains are short; and the independence of rate of oxygen concentration might be due to a compensation of deactivating processes by those leading to the production of the active centres.

If it is assumed that the active agency in the chains is an oxygenated dimethylzinc, a series of elementary processes may be visualised which lead to the following value for the rate of the reaction :

$$\text{rate} = \frac{k_1k_4[\mathrm{Zn(CH_3)_2}]^2[\mathrm{O_2}]}{k_2 + k_7 + k_3[\mathrm{O_2}] + k_6[\mathrm{N_2}] - \alpha k_4[\mathrm{Zn(CH_3)_2}] - \beta k_5[\mathrm{Zn(CH_3)_2O_2}]}.$$

In the deduction of this expression it is assumed that dimethylzinc peroxide, $ZnMe_2O_2$, is first formed in the gas; the question as to whether such a binary collision can be fruitful without the intervention of a third body is for the moment ignored, since in any case there will be a thermal equilibrium between dimethylzinc, oxygen, and the peroxide. The active centres are regarded as being deactivated by collision with oxygen or with nitrogen in the gas or on the vessel walls. Collision of the active centres with dimethylzinc leads to reaction and a propagation of the chain (α); collision with each other also leads to products and probably chain propagation too (β). It may be that the collisions of the peroxide with dimethylzinc lead to methylzinc methoxide—the product of the slow reaction—whereas interaction of two peroxide molecules gives rise to the products of the explosion; the probability of collisions between the peroxide molecules will be small at the lower and only important at the higher pressures.

The above expression, although it may not be complete, indicates the manner in which a limit phenomenon may arise. When, with increasing pressure, α or β or both attain the necessary value, the denominator may become zero and the rate infinite. The restoration of a finite rate by added inert gases is also explained.

But there is a very important difficulty in this theory, *viz.*, that the rate of the measurable reaction should be proportional to a power of the dimethylzinc concentration higher than the first, and it should also depend upon the oxygen concentration; this is not in conformity with our results (see p. 749). The following modification of the above hypothesis is therefore suggested. The active centres are indeed the peroxide molecules, but these are first formed by a collision of dimethylzinc with oxygen on the wall. It is becoming increasingly evident that such a process, in which reaction centres are formed at and then leave a surface, is common among chain reactions (Melville, *Proc. Roy. Soc.*, 1932, **135**, *A*, 315; Taylor, *Chem. Rev.*, 1931, **9**, 12). The relative adsorbabilities of the reactants on the wall will now become significant, and if the rate of the measurable reaction is determined largely by the rate of production of the active centres, subsequent processes being faster, it is possible to understand the apparent " order " of the process. Alternatively, if the rate of production of the peroxide molecules is constant, the reaction velocity will be proportional to the rate at which these collide with dimethylzinc, and hence proportional to the pressure of the latter. The rapid transition to explosion could still be explained as due to the production of branching chains when the concentration of peroxide becomes too big.

This idea has the advantage that it explains the induction period, which would be the time essential for the establishment of adsorption equilibria; and it also suggests why the rate, at first abnormally small in a clean vessel, steadily rises to a constant value as the vessel becomes dirty.

Many alternative theories have been considered, but none is so satisfactory. It does not seem possible to discard the idea of reaction chains in favour of a purely " thermal " process, for this would fail to interpret many of the facts; inert gases do not apparently function by virtue of their thermal conductivities alone; moreover, in a reaction of such a low temperature coefficient, *i.e.*, low critical increment, it seems likely that increase of the reaction velocity steadily up to that required for ignition would involve an unusually large degree of local heating. In reactions of this kind, where solid products are formed, it is conceivable that nuclei are first formed in the gas and catalyse the process, and it would be reasonable to suppose that the dimethylzinc reacts with the solid nuclei; such a mechanism would explain some of the phenomena observed, but it involves considerable difficulties and does not appear to be applicable.

SUMMARY.

The oxidation of dimethylzinc vapour has been studied kinetically. At very low pressures there is an extremely rapid oxidation, methylzinc methoxide being the final product. Thus the process is not a simple oxidation of alkyl groups. At higher pressures an explosive decomposition of the oxygenated compounds occurs, the principal products in which are carbon monoxide, methane, and hydrogen.

The rate of the measurable reaction is independent of the oxygen concentration and proportional to that of dimethylzinc; it is unaffected by the addition of inert gases and only very slightly increased by increase in temperature. It is not much influenced by vessel dimensions.

For the explosion, there is, if the dimethylzinc pressure is above a certain minimum, for any given pressure of dimethylzinc, a critical pressure of oxygen, and *vice versa*. The plot of dimethylzinc concentration against that of oxygen is displaced to lower values with increasing temperature, or with increase in diameter of the cylindrical reaction vessel. Inert gases affect the critical explosion pressures in a peculiar manner: for any given dimethylzinc concentration the requisite oxygen concentration is at first not much changed by the presence of the inert gas, but at higher concentrations of the diluent there is a rather sudden increase in the oxygen pressure needed for explosion.

It is suggested that reaction chains are involved. These are formed when active centres of a peroxidic nature, formed on the surface, escape into the gas. Under certain conditions the chains may branch and the reaction velocity become infinite. Attention is drawn to the extreme rapidity of the measurable process and its possible analogies with the reactions occurring in the highly diluted flames studied by Polanyi and his co-workers. The possibility that solid nuclei play a part in reactions of this kind is mentioned but rejected for this reaction.

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