187. *The Oxidation of Diethylzinc.*

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WITH the objects outlined in the preceding paper, the oxidation of diethylzinc has been studied. Since a more elaborate technique will be necessary to obtain fuller data, it seems desirable to summarise the results now available, especially as they throw further light upon the oxidation of dimethylzinc.

This reaction is more difficult to investigate than that with dimethylzinc. The diethyl compound boils at a much higher temperature, and accordingly its vapour pressure at room temperature is too low for experimental purposes; the liquid therefore has to be warmed in order to introduce the vapour into the reaction vessel to the desired pressure, and this causes rapid attack on the grease lubricant employed in the taps. Phosphoric acid was unsatisfactory as lubricant, and it will be necessary to design an all-glass apparatus with some form of glass valves.

The $ZnEt_2$ was supplied by Messrs. Harrington in sealed tubes, and the exptl. method was essentially as described in the foregoing paper.

The oxidation of $ZnEt_2$ proceeds at about 50° at a measurable rate, although at higher pressures of $ZnEt_2$ the rate becomes so high that reaction proceeds as the O_2 is introduced, *i.e.*, there is a type of explosion. This reaction is accompanied by a decrease in press. A sharp flash with expansion, such as was observed in the oxidation of $ZnMe_2$, is never noticed. In the measurable reaction, the product is a white solid, and, in general, the press. decrease is approx. 200% of the initial press. of $ZnEt_2$, as the following table shows :

	Initial press., mm.		Press. de-	Press. change, as %		Initial press., mm.		Press. de-	Press. change, as %
Temp.	$ZnEt_2$.	O_2.	crease.	$ZnEt_2$ press.	Temp.	$ZnEt_2$.	O_2.	crease.	$ZnEt_2$ press.
45°	5	45	9·0	180	65°	9	45	18·5	206
58	10	38	20	200	65	12	51	25	208
60	7·5	42	14	187	70	5	45	10	200
60	8	37	14·5	178	70	7	42	12·5	179

This result is in accord with either of the final products suggested by Frankland or by Meyer, *viz.*, $Zn(OEt)_2$ and $ZnEt·O·OEt$, respectively. It therefore appears that the product is a type of peroxide $ZnEt_2O_2$, although its exact structural formula is indefinite. There is here a difference from the oxidation of $ZnMe_2$, where the final product of the measurable reaction was ZnMe·OMe.

The measurable reaction of $ZnEt_2$ with O_2 is followed by a very slow press. increase, only appreciable at higher temps.; this is probably due to the decomp. of the peroxide.

Although the data are fragmentary, the measurable reaction appears to have an " order " of approx. unity with respect to $ZnEt_2$ and zero with respect to O_2. It is preceded by an induction period. Measurement made over the range 45—70° indicate an energy of activation of the order 15,000—20,000 cals.

As examples of the course of the reaction, the following two runs at 60° are given :

$ZnEt_2$, 9 mm.; O_2, 45 mm.

Time, secs.	Press. decrease.	Time, secs.	Press. decrease.
6	start	90	14
8	1	120	15·5
15	5	150	16
25	8	180	16·5
36	10	255	18
58	12	540	18·5

$ZnEt_2$, 12 mm.; O_2, 51 mm.

Time, secs.	Press. decrease.	Time, secs.	Press. decrease.
3	start	82	18·5
5	1	105	20·5
13	6	120	21·5
19	8	145	22
25	10	185	23·5
35	13	250	24·5
45	15	305	25
60	17	480	25

Although below certain pressures of $ZnEt_2$ the 200% press. decrease described above occurs, yet with higher initial pressures the press. decrease on adding O_2 is much diminished. Investigation by introduction of a known press. of O_2 (as described on p. 754 of preceding paper) showed that when addition was complete the total press. in the reaction vessel was less than the sum of the individual pressures. It appears that above a certain concn. of $ZnEt_2$ the reaction is so rapid that it is almost completed as the O_2 is introduced. The important point is that no increase of press. corresponding to that in the " explosion " of $ZnMe_2$ with O_2 occurs. There is apparently no explosive decomp. of the primary products.

Discussion.—A discussion of the above data in relation to the oxidation of dimethylzinc is interesting. Diethylzinc appears to react with oxygen directly, the resulting peroxide being stable and constituting the final product. The nature of the process and its " order " suggest that it occurs largely on the vessel walls. If active peroxide molecules escape into the gas, they do not react further with diethylzinc, *i.e.*, chains are not set up in the gas. This may explain why the process is slower than that with dimethylzinc. The latter process was largely determined by chains in the gas, and had a small heat of activation; the present reaction has a much higher energy of activation. The absence of reaction chains in the gas may explain the failure to observe explosion phenomena leading to decomposition of the primary products.

It is of interest that the literature records a decrease in " explosibility " of alkylzincs as the number of carbon atoms in the alkyl radical increases.

SUMMARY.

The product of the oxidation of diethylzinc is a solid of formula $Zn(C_2H_5)_2O_2$. The process appears to occur largely on the vessel walls, has a " total " order of approximately unity, and an energy of activation of 15,000—20,000 cals. The peroxide does not apparently set up reaction chains in the gas, in contrast with the mechanism in the oxidation of dimethylzinc. Explosion phenomena of the type observed in the latter case are absent here.

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