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Investigations on the oxidation of triethylaluminium

Several authors have recently stated[1,2,3] that the oxidation of aluminium alkyls and other metal alkyls does not take place as a simple incorporation of oxygen between the metal atom and the alkyl group, to form the metal alkoxide, as has been previously assumed. In the oxidation of trimethylaluminium, Cullis *et al.*[3] observed the formation of some hydrogen and methane, and we have noticed similar phenomena with triethylaluminium (TEA).

To get further information about the mechanism of oxidation, an air titration method was developed for following the formation of various reaction products. It was found that:

(a) TEA instantaneously reacts with oxygen even in a dilute solution. The oxygen content of the escaping gas is small.

(b) The rapid portion of the reaction of TEA with oxygen ends at a definite point at which oxygen suddenly appears in the escaping gas (Fig. 1.)

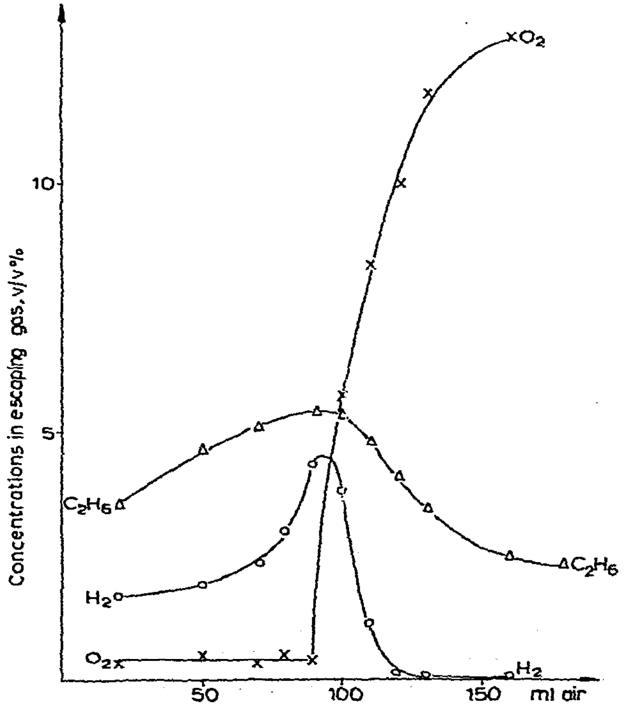

Fig. 1.

(c) The amount of oxygen used during the instantaneous reaction is somewhat less than one-third of one equivalent of the TEA used. Thus this reaction corresponds to the oxidation of one of the three alkyl groups in the molecule. Diethyl monoethoxy aluminium reacts with oxygen much more slowly, and the oxidation can be completed only by heating or using pure oxygen[4]. (Deviation of the oxygen consumption from the exact one-third equivalent is due to the inevitable contamination of TEA caused by previous oxidation and hydrolysis.)

(d) During the oxidation, hydrogen is formed. Its maximum concentration in the escaping gas appears at the point of break-through of the oxygen. After the maximum the concentration of hydrogen falls rapidly, and hydrogen essentially disappears from the gas.

(e) During the oxidation ethane and ethylene are formed (the latter in lower concentration by an order magnitude). The concentration maximum of ethane approximately coincides with that of hydrogen, although it is not as sharp or reproducible. After the maximum the concentration of ethane decreases more slowly than that of hydrogen.

To illustrate the reproducibility of this titration, nine measurements were carried out with the same partially oxidised TEA. The average percentage of intact trialkyl in the sample calculated from the oxygen consumption before the break-through point was 76.3, with a standard deviation of 4.7. Disregarding, however, the two strikingly deviating values 69.0 and 85.5, the average would be 76.0 with a standard deviation of 2.5. Considering the sensitivity of the material and the complexity of the operations, the agreement is good.

As a control, the same TEA was reacted with ethanol: according to the following equation:

$$(C_2H_5)_3Al+C_2H_5OH \rightarrow (C_2H_5)_2AlOC_2H_5+C_2H_6$$

The titration with air after the addition of ethanol resulted in a reduction of the oxygen consumption equivalent to the amount of ethanol (Table 1).

TABLE 1

RESULTS OF THE TITRATION WITH AIR OF TRIETHYLALUMINIUM AFTER ADDITION OF ETHANOL

Amount of ethanol (equivalent percentage of TEA sample)	*Oxygen consumption (equivalent percentage of TEA sample)*	*Total reacted TEA (percent of the sample)*
20	55	75
41	32	73
43	31	74
83	—	< 83

When more ethanol had been added than that equivalent to 76 per cent of the sample, the oxygen titration curve began immediately with the steeply rising part.

The appearance of hydrogen and ethane in the oxidation cannot yet be explained. These gases cannot be derived from the reaction with the humidity of air since dried air was used with 0.5 g/m^3 water content and the amount of introduced water is about 50 times less than the amount equivalent to the released gases.

The similar course of generation of hydrogen and ethane suggests that a relationship may exist between them. According to the mechanism suggested for trimethylaluminium[3] the formation of ethane may require hydrogen. It cannot, therefore, be decided whether the more rapid decrease of hydrogen after the maximum is due to the consumption of hydrogen by the simultaneous formation of ethane or only occurs because the solubility of ethane in n-heptane is much higher than that of hydrogen.

Further investigations are planned for clarifying the mechanism of this reaction.

Research Institute for the
Plastics Industry,
Budapest

A. GRÖBLER
A. SIMON
T. KADA
L. FAZAKAS

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