CHEMISTRY

Corresponding Member of the Academy of Sciences of the USSR G. A. RAZUVAEV, A. I. GRAEVSKII,

1963

SovietRxiv

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Abstract

Full Text

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ON THE OXIDATION OF ALUMINUM ALKYLS

At the present time, aluminum alkyls have found application in delicate processes of organic synthesis and polymerization. Meanwhile, the synthesis of pure aluminum alkyls and their derivatives is a very complex operation. Their extremely easy oxidizability leads to the fact that in the course of synthesis, even when special precautionary measures are observed, part of the aluminum alkyl is oxidized, and therefore it contains some admixture of oxidation products, which exert a harmful influence in the practical use of aluminum alkyls in a number of processes. On the other hand, the large-scale synthesis of various aliphatic alcohols has been carried out through the oxidation of organoaluminum compounds ([1]). Nevertheless, the oxidation of aluminum alkyls has so far practically not been studied ([2]), and in connection with this it seemed of interest to us to investigate this process.

When carrying out the oxidation of solutions of triethylaluminum (TEA) and its derivatives in *n*-heptane at various temperatures and concentrations, in a bubbling-type column with dry oxygen (dew point –60°), unstable peroxide compounds were found in considerable amounts, with a greater yield the lower the solution concentration and the reaction temperature. The final products of oxidation were two products. Under ordinary conditions (20–50°) the principal product of the reaction was diethylaluminum ethoxide (monoethoxide). At lowered temperatures (−20°)–(−30°), ethyldiethoxyaluminum (diethoxide) was formed mainly. In both cases, the oxidation was carried out until complete exhaustion of TEA in the system, which was monitored by an indicator method ([3]).

Fig. 1. Change in conductivity during oxidation of triethylaluminum

If oxidation is continued further (i.e., after all the triethylaluminum has been consumed), it can be found that at temperatures of 20–50° the monoethoxide formed is converted, with vigorous heat evolution, into the diethoxide, and the

latter, in turn, is oxidized to triethoxyaluminum. The change in conductivity during the course of oxidation gives the curve shown in Fig. 1.

In what follows we consider only the first stage of oxidation: oxidation until triethylaluminum in the system is exhausted.

The first stage of the oxidation reaction of TEA under any experimental conditions should be regarded as the formation of the aluminum salt of ethyl hydroperoxide

$$Al(C_2H_5)_3 + O_2 \rightarrow Al(C_2H_5)_2OOC_2H_5. \quad (1)$$

This assumption is in good agreement with the results of hydrolysis of TEA oxidation products at low temperatures, as a result of which ethyl hydroperoxide, ethane, and aluminum hydroxide were identified. The peroxide organoaluminum compound decomposes, interacting with the initial aluminum alkyl to form the monoethoxide, while

at room temperature this reaction proceeds at an extremely high rate.

A detailed study of the oxidation of TEA showed that this process obeys very complex regularities.

It turned out that the monoethoxide, which is the principal product of TEA oxidation at room temperatures, is very reactive and, as soon as it is formed, again enters into reaction with oxygen. Oxidation of the monoethoxide begins even before all the triethylaluminum has been consumed, and therefore both groups of processes occur simultaneously in the reaction volume: oxidation of triethylaluminum itself and oxidation of the monoethoxide. The latter reaction proceeds at a high rate and leads to the formation of peroxide organoaluminum compounds that are sufficiently stable at low temperatures (Fig. 2, 1), but readily decompose in the presence of the initial TEA (Fig. 2, 3) or monoethoxide (Fig. 2, 3).

Thus, the occurrence of the following reactions may be stated:

$$Al(C_2H_5)_2OC_2H_5 + O_2 \rightarrow AlC_2H_5(OC_2H_5)OOC_2H_5, \quad (2)$$

$$AlC_2H_5(OC_2H_5)OOC_2H_5 + Al(C_2H_5)_3 \rightarrow$$

$$\rightarrow Al(C_2H_5)_2OC_2H_5 + AlC_2H_5(OC_2H_5)_2, \quad (3)$$

$$AlC_2H_5(OC_2H_5)OOC_2H_5 + Al(C_2H_5)_2OC_2H_5 \rightarrow$$

Fig. 2. Decomposition of an organoaluminum peroxide obtained by oxidation of the monoethoxide. 1—without additives, 2—with addition of TEA, 3—with addition of monoethoxide

Figure 2: Fig. 2. Decomposition of an organoaluminum peroxide obtained by oxidation of the monoethoxide. 1—without additives, 2—with addition of TEA, 3—with addition of monoethoxide

$$\rightarrow 2AlC_2H_5(OC_2H_5)_2. \quad (4)$$

Fig. 2. Decomposition of an organoaluminum peroxide obtained by oxidation of the monoethoxide. 1—without additives, 2—with addition of TEA, 3—with addition of monoethoxide.

At room temperature the rate of decomposition of the peroxide considerably exceeds the rate of oxidation of the monoethoxide.

The diethoxide formed as a result of act (4), in turn, is oxidized to the peroxide compound

$$AlC_2H_5(OC_2H_5)_2 + O_2 \rightarrow Al(OC_2H_5)_2OOC_2H_5. \quad (5)$$

However, this process proceeds at a very low rate. By measuring the reaction rates in a simple inertialess apparatus that makes it possible to study gas absorption in very rapid processes, it was shown that the rate constants for oxidation of TEA, monoethoxide, and diethoxide are related as follows:

$$K_1 : K_2 : K_5 = 100 : 26 : 0.96.$$

Consequently, reactions (1) and (2) proceed at commensurable rates, whereas consumption of the diethoxide according to reaction (5) is greatly retarded and takes place at a rate two orders of magnitude lower than the rate of reaction (1).

Under these conditions, rapid oxidation of TEA and monoethoxide should occur with simultaneous accumulation of diethoxide in the system. This conclusion was consistent with experimental data, according to which the principal product of the TEA oxidation reaction at low temperatures was indeed the diethoxide, its accumulation in the reacting system being a direct consequence of the competition of several reactions proceeding at different rates. At the same time, the result obtained was in contradiction with another experimental fact, according to which at room temperatures the main product of the reaction (as long as TEA is present in the reaction medium) is the monoethoxide.

In this connection it may be supposed that the diethoxide, as soon as it appears, takes part in some secondary process proceeding at a sufficiently—

at a sufficiently high rate at room temperature. Such a process proved to be the exchange process between diethoxide and TEA (step 6)

$$Al(C_2H_5)_3 + AlC_2H_5(OC_2H_5)_2 \rightarrow 2Al(C_2H_5)OC_2H_5. \quad (6)$$

The study of this reaction by means of the indicator method showed that it proceeds rather rapidly already at 5–10°C, and at 40–50°C exchange occurs almost instantaneously.

As the temperature is lowered the reaction is retarded, so that at −30° a mixture of TEA and diethoxide does not disproportionate to completion even over 25 hours. Nevertheless, the existence of stage (6) in the scheme of TEA oxidation, and consequently its influence on the course of the oxidation process at low and high temperatures, remained, in our view, hypothetical until another reaction was found, analogous to the first but, in contrast to it, proceeding at a high rate only at temperatures above 100°C. This reaction proved to be the disproportionation reaction of diethylaluminum bromide (monobromide) and diethoxyaluminum bromide (diethoxybromide)

$$Al(C_2H_5)_2Br + Al(OC_2H_5)_2Br \rightarrow 2AlC_2H_5(OC_2H_5)Br. \quad (7)$$

As was found, the oxidation of monobromide basically obeys the regularities characteristic of TEA oxidation. However, the practical absence of a disproportionation stage between monobromide and diethoxybromide at room temperatures changed the direction of the process and the composition of the final products. It was found that, when monobromide is oxidized with the use of the indicator method of control, over the entire temperature interval from −30° to +30°C the main product of the reaction is diethoxide.

Thus, it seems possible to us to propose the following scheme of the main processes occurring simultaneously in the reaction volume during TEA oxidation:

(I) $Al(C_2H_5)_3 + O_2 \rightarrow Al(C_2H_5)_2OOC_2H_5$ very rapidly,
$Al(C_2H_5)_2OOC_2H_5 + Al(C_2H_5)_3 \rightarrow 2Al(C_2H_5)_2OC_2H_5$ very rapidly,

(II) $Al(C_2H_5)_2OC_2H_5 + O_2 \rightarrow AlC_2H_5(OC_2H_5)_2OOC_2H_5$ rapidly,

$AlC_2H_5(OC_2H_5)OOC_2H_5 \xrightarrow{+Al(C_2H_5)_3} Al(C_2H_5)_2OC_2H_5 + AlC_2H_5(OC_2H_5)_2$ very rapidly,

$AlC_2H_5(OC_2H_5)OOC_2H_5 \xrightarrow[AlC_2H_5OC_2H_5]{} 2AlC_2H_5(OC_2H_5)_2$ very rapidly,

(III) $AlC_2H_5(OC_2H_5)_2 + O_2 \rightarrow Al(OC_2H_5)_2OOC_2H_5$ slowly,
(IV), $AlC_2H_5(OC_2H_5)_2 + Al(C_2H_5)_3 + 2Al(C_2H_5)_2 \rightarrow 2Al(C_2H_5)_2OC_2H_5$.

The rate of the steps of stage (IV) depends on the reaction conditions ([3]), primarily on temperature.

It should be noted that, simultaneously with the main processes represented in the scheme, during TEA oxidation there also occurs a series of side and secondary processes. For example, we have shown that, together with aluminum alkoxide and peroxide derivatives, small amounts of ethane and ethylene are always detected (2–3% of the total amount of the main products).

The study of interactions in model systems containing, on the one hand, diethoxyperoxycumylaluminum and, on the other hand, TEA, monoxide, or dioxide showed that the evolution of gaseous products is in a definite way associated with the radical reaction of organoaluminum peroxides with aluminum alkyls.

Received
25 XII 1962

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Note: Figure translations are in progress. See original paper for figures.