Reports of the Academy of Sciences of the USSR

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1957

SovietRxiv

Abstract

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Reports of the Academy of Sciences of the USSR

1957. Volume 113, No. 3

CHEMISTRY

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ON THE VAPOR-PHASE OXIDATION OF STYRENE AND α-METHYLSTYRENE ON TIN VANADATE

(Presented by Academician B. A. Arbuzov, 3 X 1956)

The study of oxidative transformations of unsaturated compounds under the action of molecular oxygen in the presence of heterogeneous catalysts is of great importance for elucidating the mechanism of catalytic oxidation reactions of organic compounds, which at present have become widely used in the organic-synthesis industry. Of definite interest in this respect should be the study of vapor-phase catalytic oxidation of aromatic compounds with a double bond in the side chain, since they are probable intermediate products in the oxidation of alkylbenzenes ([1]). The literature on this question is extremely scanty; in particular, we were unable to find any information on the vapor-phase oxidation of the objects of the present study—styrene and α-methylstyrene—by atmospheric oxygen on vanadium catalysts.

The starting substances used by us had the following characteristics: styrene—b.p. 52°/28 mm, $n_D^{20} = 1.5460$, $d_4^{20} = 0.909$; α-methylstyrene—b.p. 62°/20 mm, $n_D^{17.5} = 1.5381$, $d_4^{20} = 0.897$. The experiments were carried out in a flow-type apparatus with a contact time of 0.08–0.10 sec and a space velocity of 0.10–0.12. Moist air containing up to 300 g/m^3 of water was used as the oxidizing agent. Granulated tin vanadate served as the catalyst.

The main oxidation products of both hydrocarbons studied were benzoic acid and maleic anhydride. Their determination was carried out by the usual method, titration with alkali ([2]). In separate experiments, for control, they were isolated in pure form. Along with the acids, quinone, formaldehyde, carbon monoxide, and carbon dioxide were present in the reaction products of all experiments. In addition, benzaldehyde was found in the oxidation of styrene, and acetophenone in experiments with α-methylstyrene. Quinone was determined quantitatively by the iodometric method (³), and was identified by the formation of quinhydrone with m.p. 171°. Quantitative determination of formaldehyde was based on the reaction forming formaldimedone (m.p. 187°). Benzaldehyde and acetophenone were isolated by distillation of the oily reaction products that had first been washed with soda and dried. Benzaldehyde had b.p. 176°/700 mm, $n_D^{20} = 1.5459$; its semicarbazone melted at 220–221°. Acetophenone boiled at 98°/35 mm and had $n_D^{20} = 1.5347$; the derivative with semicarbazide melted at 196°. Determination of CO and CO_2 was carried out by the usual gas-analysis procedure on a VTI apparatus.

The results of the experiments on oxidation of styrene and α-methylstyrene are presented in Tables 1 and 2. As is seen from the data given, the yield of individual oxidation products of each of the starting substances depends on the reaction temperature: an increase in it promoted gradual destruction of the carbon skeleton of the oxidized compound. Thus, in experiments carried out at ot-

at a relatively low temperature, the reaction products were dominated by carbonyl compounds with an unchanged aromatic ring and by benzoic acid. With increasing temperature, their yield decreased and the amount of quinone and maleic anhydride increased.

A very characteristic indicator is the amount of low-molecular-weight products of complete and incomplete oxidation that are formed. As can be seen from the data presented, the total amount of formaldehyde, CO, and CO_2 at low temperatures does not exceed 1.25 mol per 1 mol of hydrocarbon oxidized. This indicates that the low-molecular-weight products are formed chiefly at the expense of cleavage of side groups. At high temperatures the amount of low-molecular-weight products reaches 2.4 mol/mol (in the case of α-methylstyrene). Under these conditions, part of the low-molecular-weight products is formed through destruction of the benzene ring with formation of maleic anhydride and products of its decomposition. It should be noted that among the low-molecular-weight products the principal one is carbon monoxide, which indicates its high stability under the reaction conditions.

Table 1

Yield of the principal oxidation products of styrene

Experiment No.	Temperature, °C	Benzaldehyde	Benzoic acid	Quinone	Maleic anhydride
1	285	7.8	30.3	undetermined	5.3
2	309	3.3	53.4	0.5	6.4
3	320	traces	54.5	0.7	9.6
4*	330	»	57.8	0.3	11.4
5	340	»	57.1	0.8	10.5
6	350	»	48.8	0.8	10.9
7	360	»	43.0	0.7	13.3

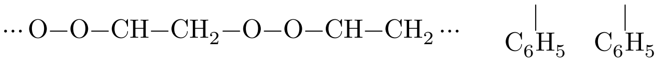
Experiment No.	Temperature, °C	Benzaldehyde	Benzoic acid	Quinone	Maleic anhydride
8**	374	»	35.0	0.7	12.7
9	385	»	31.8	0.2	17.3
10	400	»	23.1	0.1	15.6

Yield of products of incomplete oxidation, in % of theory based on the converted starting material.

* In experiment No. 4, formaldehyde (0.11 mol/mol styrene), carbon monoxide (0.96 mol/mol), and carbon dioxide (0.12 mol/mol) were also determined.

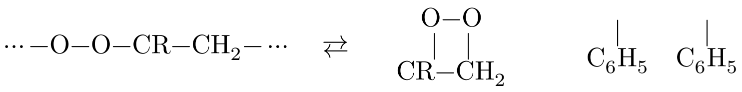
** In experiment No. 8, formaldehyde (0.09 mol/mol), carbon monoxide (1.06 mol/mol), and carbon dioxide (0.42 mol/mol) were found.

The results obtained give grounds for assuming that the oxidation of styrene and α-methylstyrene in the vapor phase over tin vanadate in the initial stages proceeds in the same direction as in the condensed phase in the presence or absence of catalysts (4, 5). There are indications (6) that, under mild conditions and in the absence of catalysts, the interaction of styrene with molecular oxygen leads to the formation of a polymeric peroxide of the type



$$\cdots O{-}O{-}\underset{C_6H_5}{CH}{-}CH_2{-}O{-}O{-}\underset{C_6H_5}{CH}{-}CH_2\cdots$$

It is quite probable that the initial stage in the formation of such a peroxide is the addition of oxygen to the styrene or α-methylstyrene molecule with formation of unstable peroxides of the following structure:



$$\cdots{-}O{-}O{-}\underset{C_6H_5}{CR}{-}CH_2{-}\cdots \rightleftarrows \begin{array}{c} O{-}O \\ |\quad | \\ \underset{C_6H_5}{CR}{-}CH_2 \end{array}$$

where: $R = H, CH_3$.

Under vapor-phase oxidation conditions, formation of a polymeric peroxide is impossible because of the high temperature and the low concentration of the reacting components. More probable is thermal decomposition with formation of benzaldehyde and formaldehyde in the case of styrene, and acetophenone

and formaldehyde—in the case of methylstyrene. The experimental data given in Tables 1 and 2 confirm this assumption. At relatively low—

Table 2

Yield of the main oxidation products of α-methylstyrene

Run No.	Reaction temperature, °C	Acetophenone, % of theory	Benzoic acid, % of theory	Quinone, % of theory	Maleic anhydride, % of theory	CH_2O, mol per mol of initial substance	CO, mol per mol of initial substance	CO_2, mol per mol of initial substance
11	310	9.4	25.2	0.2	10.1	not det.	not det.	not det.
12	330	2.3	54.3	0.7	17.5	0.22	0.88	0.15
13	342	traces	61.2	1.1	16.6	0.24	1.31	0.11
14	354	»	56.0	1.4	18.0	0.24	1.54	0.14
15	366	»	47.5	1.4	20.6	0.28	1.69	0.18
16	378	»	44.5	1.8	22.8	0.25	1.93	0.16
17	390	»	40.0	1.8	23.8	0.23	1.95	0.20

reaction temperatures, appreciable quantities of the expected products of transformation of monomeric peroxides can be isolated from the catalyst.

At higher temperatures it is not possible to detect acetophenone or benzaldehyde in the reaction products, since their further oxidation occurs, with subsequent conversion into benzoic acid, benzoquinone, and maleic anhydride ([1], [2]).

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Received
29 IX 1956

CITED LITERATURE

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