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V. L. ANTONOVSKII and B. I. MAKHALETS

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Abstract

Full Text

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ON THE SEQUENCE OF FORMATION OF PRODUCTS DURING LIQUID-PHASE OXIDATION OF CUMENE

(Presented by Academician N. N. Semenov, 5 V 1961)

The mechanism of oxidation of cumene to hydroperoxide has not been sufficiently studied, although this process has been carried out on an industrial scale.

Determining the nature of the accumulation of various side products of the reaction under conditions close to industrial ones may have practical significance, since it would make it possible to reduce the consumption coefficient of benzene in the production of phenol and acetone by the cumene method.

Fig. 1. *a* –dependence of the yield of acetophenone (1) and DMPC (2) on the depth of oxidation of cumene; *b* –kinetics of accumulation of cumene hydroperoxide

Fig. 2. Formation of acetophenone (1) and DMPC (2) during decomposition of oxidate containing 34% hydroperoxide, 1.6% DMPC, and 1.2% acetophenone

To clarify the pathways of formation of acetophenone and dimethylphenylcarbinol (DMPC), the present work studied the kinetics of accumulation of these products during oxidation of cumene to hydroperoxide.

Cumene of plant manufacture, obtained by alkylation of benzene with propylene over aluminum chloride, distilled and washed with a 5% alkali solution, was oxidized with air in a bubbling reactor made of stainless steel. The reaction temperature was 115°, the pressure atmospheric, and the air feed rate was 150 volumes per 1 volume of cumene per hour. During the reaction, samples were taken in which hydroperoxide and cumene peroxide, acetophenone, and DMPC were determined. Analyses for hydroperoxide and peroxide (separately) were performed iodometrically, for acetophenone polarographically, and for DMPC by IR spectra. The last two methods were developed specially for analyses in the presence of large amounts of hydroperoxide.

Figure 1*a* presents the accumulation curves of acetophenone and DMPC as a function of the reaction depth (percent hydroperoxide). The concentration of acetophenone, as is evident from the graph, increases linearly with the depth of the process.

The ratio [acetophenone] : [hydroperoxide] remains constant throughout the entire course of the reaction and is equal to 0.03. Such a regularity is characteristic of products formed in parallel.

The accumulation of DMPC has an autocatalytic character. The presence of an "induction period" —appreciable amounts of DMPC are detected only after the accumulation of about 10% cumene hydroperoxide—and the progressive increase in the ratio [DMPC] : [hydroperoxide] with the depth of reaction indicate that DMPC is a product of hydroperoxide decomposition. The results of experiments on the thermal decomposition of oxidized cumene lead to analogous conclusions. Decomposition of the oxidate was carried out in glass ampoules from which air had been removed, at 115°. The analytical results are presented in the form of a graph (Fig. 2). The constancy of the acetophenone concentration and the increase in the DMPC concentration confirm the conclusion that, during cumene oxidation, acetophenone is not formed from cumene hydroperoxide, whereas DMPC is a product of the decomposition of the latter.

The absence of any noticeable new formation of acetophenone during the thermal decomposition of an oxidate containing 34% cumene hydroperoxide indicates that the reaction:

$$C_6H_5C(CH_3)_2O\cdot + C_6H_5CH(CH_3)_2 \rightarrow C_6H_5C(CH_3)_2OH + C_6H_5C(CH_3)_2$$

at 115° proceeds at a substantially higher rate than the monomolecular decomposition:

$$C_6H_5C(CH_3)_2O \rightarrow CH_3O + C_6H_5COCH_3.$$

Cumene peroxide, as the analytical results showed, is formed in an amount of no more than 0.5% when the hydrocarbon is oxidized to a depth of 25-30%

hydroperoxide. Evidently it is a product of recombination of oxy- or peroxy-radicals. In still smaller amounts (less than 0.1%), at the same depths of oxidation, α-methylstyrene was detected.

The experimental results obtained make it possible to draw certain conclusions concerning the mechanism of the cumene oxidation reaction. From Fig. 1b it is evident that, with the exception of a short initial period, the reaction rate is constant. This indicates the constancy of the composition and concentration of the radicals propagating chain (2) within the oxidation depths studied.

From general theoretical concepts of radical-chain processes it is known (^{3}) that hydroperoxide formation occurs as a result of the alternation of two elementary steps:

$$R\cdot + O_2 \rightarrow RO_2\cdot, \tag{1}$$

$$RO_2\cdot + RH \rightarrow RO_2H + R\cdot\,. \tag{2}$$

The parallel formation of acetophenone and hydroperoxide that we have found is a consequence of the transformation, competing with reaction (2), of the radical $C_6H_5C(CH_3)_2OO\cdot$ directly into acetophenone.

In the literature the question has been discussed of possible reactions involving the radical $C_6H_5C(CH_3)_2OO\cdot$, in addition to its interaction with the starting hydrocarbon. One group of transformations is associated with chain termination ($^{4-6}$). In another group of transformations, the possibility is postulated of chain continuation with the formation of a stable product of nonperoxidic character (^{5,6}). Of the two possible reactions as a result of which acetophenone is formed:

$$\begin{aligned} 2C_6H_5C(CH_3)_2OO\cdot \rightarrow\ & 2C_6H_5C(CH_3)_2O\cdot + O_2, \\ & C_6H_5COCH_3 + CH_3\cdot \end{aligned}$$

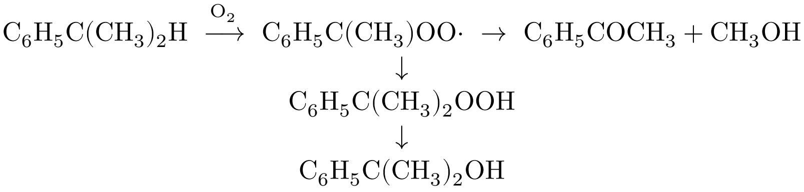
$$C_6H_5C(CH_3)_2O\cdot \begin{array}{l} \nearrow \\ \searrow^{+RH} \end{array} \begin{array}{c} C_6H_5COCH_3 + CH_3\cdot \\ C_6H_5C(CH_3)_2OH \end{array} \tag{I}$$

$$2C_6H_5C(CH_3)_2OO\cdot \rightarrow [C_6H_5C(CH_3)_2OOOO(CH_3)_2CC_6H_5]$$

$$\begin{array}{c} C_6H_5C(CH_3)_2OO(CH_3)_2C{-}C_6H_5 + O_2 \\ \downarrow \\ 2C_6H_5COCH_3 + CH_3OO\cdot + CH_3\cdot \end{array} \tag{II}$$

under our conditions, as follows from the experimental data, only reaction (II) takes place.

Thus, in the oxidation of cumene by air at 115°, the following sequence of formation of the main reaction products occurs:



$$\begin{tikzcd}
C_6H_5C(CH_3)_2H \arrow[r, "O_2"] & C_6H_5C(CH_3)OO\cdot \arrow[r] \arrow[d] & C_6H_5COCH_3 + CH_3OH \\
& C_6H_5C(CH_3)_2OOH \arrow[d] & \\
& C_6H_5C(CH_3)_2OH &
\end{tikzcd}$$

Branch of the Scientific-Research Institute of Synthetic Alcohols and Organic Products
Novo-Kuibyshevsk

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