# CHEMISTRY

Academician A. V. TOPCHIEV, I. F. BAEV, and L. A. MOROZOV

1958

SovietRxiv

## Abstract

## Full Text

*CHEMISTRY*

Academician A. V. TOPCHIEV, I. F. BAEV, and L. A. MOROZOV

# SYNTHESIS OF MONO- AND DIHYDROPEROXIDES OF *p*-DIISOPROPYLBENZENE

Industrial methods for obtaining alkylbenzenes do not always make it possible to obtain an alkylate suitable for liquid-phase oxidation. In this connection, the construction of large-scale production facilities was determined by the technology for the synthesis of isopropylbenzene from benzene and propylene in the presence of an aluminum chloride catalyst. At the first stage this ensured the successful development of joint industrial production of phenol and acetone ([1]).

It was reported earlier that, along with the study of the process of alkylating benzene with olefins in the presence of a boron fluoride catalyst ([2]), the liquid-phase oxidation of alkylbenzenes obtained by this method is also being studied ([3]). In the present communication, data are given on the liquid-phase oxidation of *p*-diisopropylbenzene obtained by the above-mentioned method.

In the process of liquid-phase oxidation of *p*-diisopropylbenzene, the formation of the mono- and dihydroperoxides proceeds in accordance with the equations:

$$(CH_3)_2CH{-}C_6H_4{-}CH(CH_3)_2 + O_2 \rightarrow (CH_3)_2COOH{-}C_6H_4{-}CH(CH_3)_2, \quad (1)$$

$$(CH_3)_2COOH{-}C_6H_4{-}CH(CH_3)_2{+}O_2 \rightarrow (CH_3)_2COOH{-}C_6H_4{-}COOH(CH_3)_2. \quad (2)$$

*p*-Diisopropylbenzene was isolated from the alkylate obtained in an installation whose productivity was 60–70 kg of isopropylbenzene and 7–10 kg/hour of *p*-diisopropylbenzene.

**Table 1**

Properties of fractions isolated from polyalkylbenzenes

| Separation conditions and properties of fractions | Fractions I | Fractions II | Bottom residue, boiling point 234–236° |
|---|---|---|---|
| Temperature at top of column, °C | 82–93 | 88–100 | |
| Pressure during collection of fraction, mm Hg | 28–40 | 13–31 | atm. |
| Fraction content, % | 22.3 | 57 | 20 |
| $d_4^{20}$ | 0.8542 | 0.8580 | 0.8628 |
| $n_D^{20}$ | 1.48926 | 1.48976 | 1.4899 |

In a material-balance experiment (No. 5), from the interaction of benzene with propylene in a ratio of 1 : 0.46 and catalyst 0.00055 mole, 2051 kg of a mixture of the following composition was obtained: unreacted benzene 38%, isopropylbenzene 50.4%, diisopropylbenzene and higher alkylbenzenes 10.6%.

From the polyalkylbenzene fraction, by vacuum rectification on a column with an efficiency of 22–25 theoretical plates, fractions were isolated whose composition is given in Table 1.

For oxidation, a preliminarily purified fraction II was used: $d_4^{20}$ 0.8585, $n_D^{20}$ 1.48982, freezing point from −20 to −23°.

The diisopropylbenzene fraction, according to its indices, did not correspond to pure *p*-diisopropylbenzene as given by Millspaugh ([4]), $d_4^{20}$ 0.85676, $n_D^{20}$ 1.48983, freezing point −17.07°. In the process of obtaining the hydroperoxide, air with an oxygen content of 21–22% was used. The oxidation was carried out in a 3-liter glass reactor equipped with a vigorously act-

equipped with a stirrer, reflux condenser, bubbler, electric coil for heating, and the corresponding measuring and control instruments.

For the experiment, 1.5 kg of diisopropylbenzene, 56 mg of divalent manganese, and 1.6 g of calcium oxide hydrate were taken. The reaction was carried out at a temperature of 112° ± 1°, an air feed rate of 65–70 l/hr, and atmospheric pressure. The formation of hydroperoxide in the reaction mass was monitored by iodometric titration and by measuring the refraction of samples taken from the reactor. The concentration of hydroperoxide in the reaction mixture was allowed to be no higher than 55% calculated as monohydroperoxide, or 25% as

dihydroperoxide. The formation of hydroperoxide in the reaction mixture as a function of reaction time is shown in Fig. 1.

In view of the fact that the oxidation of *p*-diisopropylbenzene proceeds initially with the formation of mono-, and then dihydroperoxide, the graph gives: curve 1 calculated as monohydroperoxide, and curve 2 as dihydroperoxide.

After completion of the oxidation, the resulting mixture at a temperature of 100-105° was filtered from suspended matter on a Schott filter. The reaction mixture was then separated into unreacted diisopropylbenzene, monohydroperoxide, and dihydroperoxide.

The indices of the oxidation process of diisopropylbenzene and the quality of the products obtained are given in Table 2.

**Fig. 1.** Rate of formation of hydroperoxide in the reaction mixture as a function of time. 1—calculated as monohydroperoxide, 2—calculated as dihydroperoxide of *p*-diisopropylbenzene.

The monohydroperoxide of *p*-diisopropylbenzene isolated from the reaction mixture was a colorless oily liquid with a content

**Table 2**

**Oxidation indices of the diisopropylbenzene fraction**

| | Quantity, g | Content of main substance, % | $d_4^{20}$ | $n_D^{20}$ | M.p., °C |
|---|---|---|---|---|---|
| Taken for oxidation: | | | | | |
| *p*-diisopropylbenzene | 1500 | – | 0,8585 | 1,48982 | −21 |
| air (liters) | 700 | 21 | – | – | – |
| divalent manganese | 0,056 | 6 | – | – | – |
| calcium oxide hydrate | 1,5 | 98 | – | – | – |
| Reaction mixture obtained | 1532 | 56* | – | – | – |
| Including: | | | | | |

| | Quantity, g | Content of main substance, % | $d_4^{20}$ | $n_D^{20}$ | M.p., °C |
|---|---|---|---|---|---|
| *p*-diisopropylbenzene | 651 | 98 | 0,8584 | 1,48981 | – |
| monohydroperoxide of *p*-diisopropylbenzene | 637 | 91,4 | 0,9931 | 1,51280 | – |
| dihydroperoxide of *p*-diisopropylbenzene | 200 | 96,7 | 1,272 | – | 139 |
| Diisopropylbenzene and other products from the exhaust gases | 90 | – | 0,8587 | 1,4894 | – |

* Hydroperoxide calculated as monoproduct.

of the main substance, 94.6%, boiling at a temperature of 98–112° and a residual pressure of 0.17–0.21 mm Hg, $d_4^{20}$0.9932, $n_D^{20}$1.51286. With a content of 14.1% monohydroperoxide in a solution of *p*-diisopropylbenzene, $n_D^{20}$1.4930. The monohydroperoxide was mixed with purified *p*-diisopropylbenzene in a ratio of 2 : 8 by weight and again subjected to oxidation.

The resulting dihydroperoxide was purified by recrystallization in benzene. After purification, the dihydroperoxide was a solid crystalline white substance with a content of 99.8% of the main product, m.p. 140° ± 1°; it decomposes on melting, $d_4^{20}$1.2724, $n_D^{20}$1.38326, in a 6% solution of isopropyl alcohol (pure isopropyl alcohol $n_D^{20}$1.37664).

Thus, *p*-diisopropylbenzene, obtained as a by-product with isopropylbenzene, is a good starting material for obtaining *p*-diisopropylbenzene dihydroperoxide.

Received
3 V 1957

## CITED LITERATURE

1. P. G. Sergeev, *Tr. Vsesoyuzn. soveshch. po kompleksnoi khimicheskoi pererabotke neftyanykh gazov*, 1956, pp. 362–365.

2. A. V. Topchiev, M. V. Kurashov, Ya. M. Paushkin, I. F. Faev, *Tr. Vsesoyuzn. soveshch. po kompleksnoi khimicheskoi pererabotke neftyanykh gazov*, 1956, pp. 414–421.

3. I. F. Faev, A. V. Topchiev, Ya. M. Paushkin, M. V. Kurashov, *Tr. Vsesoyuzn. soveshch. po kompleksnoi khimicheskoi pererabotke neftyanykh gazov*, 1956, pp. 422–431.

4. W. Melpolder, J. E. Woodbridge, J. E. Headington, *J. Am. Chem. Soc.*, **70**, 935 (1948).

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