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Abstract

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ON THE BY-PRODUCTS OF THE REACTION OF BENZOYL PEROXIDE WITH BENZENE

The reaction between benzoyl peroxide (BP) and benzene proceeds according to the so-called R–H scheme proposed by Gelissen and Hermans ([1])

$$[C_6H_5CO_2]_2 + C_6H_6 \begin{cases} \longrightarrow C_6H_5C_6H_5 + C_6H_5COOH + CO_2 & (1)\ \text{main} \\ \longrightarrow C_6H_5CO_2C_6H_5 + C_6H_6 + CO_2 & \text{side} \end{cases}$$

Together with diphenyl, small amounts of terphenyl and quaterphenyl are formed. The authors believe that their formation is also explained by a reaction analogous to reaction (1). This was confirmed by studies carried out between BP and diphenyl ([2]). However, in our previous work on the decomposition of BP in benzene using labeled C^{14} compounds, a discrepancy was found between the calculated and observed isotopic composition of diphenyl and quaterphenyl ([3]). An experiment repeated with labeled benzene under the conditions of Gelissen and Hermans showed that diphenyl contains 41% phenyl radicals from benzene instead of the calculated 50% (experiment 1). This value is close to the data obtained earlier ([3]),

Table 1

Reactions of benzoyl peroxide

Exp. No.	Taken into reaction: benzoyl peroxide, g	Taken into reaction: benzoyl peroxide, activity	Taken into reaction: benzene, g	Taken into reaction: benzene, activity	Taken into reaction: diphenyl, g	Taken into reaction: diphenyl, activity	Taken into reaction: terphenyl, g	Taken into reaction: terphenyl, activity	Obtained: diphenyl, g	Obtained: diphenyl, activity	Obtained: % phenyl groups from benzene	Obtained: diphenyl, g	Obtained: terphenyl, activity	Obtained: % phenyl groups	Obtained: quaterphenyl, g	Obtained: quaterphenyl, activity	Obtained: % quaterphenyl groups
1	60	—	221	925	—	—	—	—	10	377	41	0.3	273	30	0.56	445	48
2	20	—	67	825	—	—	—	—	—	—	—	—	—	—	0.12	409	50
3	10	933	32.5	—	12.9	—	—	—	13	113	—	—	—	—	0.10	505	52
4	20	—	67	—	3.5	364	—	—	—	—	—	—	—	—	0.27	1	≈ 0
5	10	—	32.5	—	—	—	0.12	150	—	—	—	—	—	—	0.10	no	no
6	7.2	—	—	—	12	220	—	—	—	—	—	0.12	150	68	0.05	112	50

Notes. 1. The quantitative yields of the products of the above reactions have been described sufficiently fully by many authors. In our experiments, the isotopic composition and purity of the products of these reactions were studied. 2. In experiment No. 3, BP containing radiocarbon in the benzene rings was used. 3. The percentage of active phenyl groups in experiments Nos. 1 and 2 was calculated relative to the initial activity of benzene; in experiment No. 3, relative to the initial activity of peroxide; and in experiments Nos. 4 and 6, relative to the initial activity of diphenyl; in experiment No. 5, relative to the activity of terphenyl. 4. Radiometric analysis of the starting products and reaction products was carried out by measuring the activity, with an internal-filling counter, of carbon dioxide obtained by combustion of the substance. The measurement error was 3%; activity is expressed in mm/min.

as well as to the results of Bagdasaryan, Milyutinskaya, and Izrailevich ( ), who used compounds labeled with deuterium. The isotopic composition of terphenyl agrees very closely with the calculation according to the equation:

$$C_6H_5C_6H_5 + (C_6H_5CO_2)_2 \rightarrow C_6H_5C_6H_4C_6H_5 + C_6H_5COOH.$$

If one assumes that the phenylation reaction proceeds further and that quaterphenyl is formed from terphenyl, then the composition of the latter should be: one phenyl nucleus from benzene and three nuclei from BP. However, the isotopic composition differs sharply from the above calculation. It was found

experimentally that quaterphenyl contains two phenyl nuclei from benzene and two from BP (experiments 1, 2). Consequently, there must be some other source of quaterphenyl formation. To test the proposed assumption, we added to the reaction mixture benzene + BP those compounds (diphenyl and terphenyl) from which quaterphenyl may be formed according to the R–H scheme. Inactive diphenyl was added to a benzene solution of labeled BP (experiment 3). If the latter is the product from which quaterphenyl is obtained, then such an addition should sharply reduce the activity of the quaterphenyl. The experiment showed that it remains practically unchanged. Completely analogous results were obtained when inactive components of active diphenyl were introduced into the reaction mixture (experiment 4). The isolated quaterphenyl contains no C^{14}. As in experiment 4, inactive quaterphenyl was obtained upon decomposition of BP in benzene in the presence of added labeled terphenyl (experiment 5).

In the interaction of BP with labeled diphenyl under the conditions of Gelissen and Hermans ([2]), the isolated terphenyl, in isotopic composition, corresponds to terphenyl containing one benzene nucleus of BP per molecule of diphenyl, while quaterphenyl contains two benzene nuclei of BP per molecule of diphenyl (experiment 6).

Recently an interesting paper by De Tar and Long ( ) was published; they succeeded in isolating from the products of the reaction of BP with benzene dihydrodiphenyl (a) and tetrahydrodiphenyl (b). Both compounds were obtained from the σ-complex of the phenyl radical with benzene. The first (a) by the reaction of hydrogen addition to the σ-complex, and the second (b) by radical recombination. Thus, the general course of the reaction of BP with benzene can be represented by the following scheme (taking into account the reaction in labeled benzene):

$$C_6H_5\cdot + {}^*C_6H_6 \longrightarrow [C_6H_5{-}{}^*C_6H_6] \longrightarrow C_6H_5{-}{}^*C_6H_6\cdot \xrightarrow[\text{-RH}]{R\cdot} C_6H_5{-}{}^*C_6H_5 \text{ (main)}$$

$$\pi\text{-complex} \qquad \sigma\text{-complex}$$

$$[\pi\text{-complex}] \longrightarrow C_6H_6 + {}^*C_6H_5\cdot$$

$$\sigma\text{-complex} \xrightarrow{\text{H-donor}} \text{dihydrodiphenyl radical}$$

$$\sigma\text{-complex} \xrightarrow{\text{Dimerization (side)}} \text{tetrahydroquaterphenyl} \xrightarrow{-HR,\ R\cdot} \text{quaterphenyl}$$

Quaterphenyl must be formed by dehydrogenation, under the action of BP or of free radicals, of tetrahydrodiphenyl. The isotopic composition of the latter agrees with the calculation according to the proposed scheme.

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