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Chemistry

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Abstract

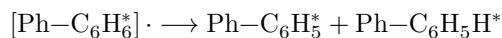
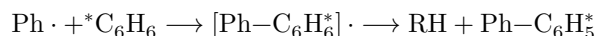
Full Text

Chemistry

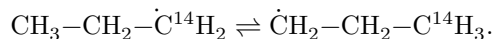
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ON THE POSSIBILITY OF ISOMERIZATION OF THE PHENYL RADICAL IN REACTIONS OF BENZOYL PEROXIDE

The mechanism of the reaction of benzoyl peroxide (BP) with benzene has been the subject of numerous studies. The great attention paid to this reaction is due to the fact that BP is one of the most widely used initiators of free-radical reactions and, moreover, serves as a convenient object for investigating a number of theoretical questions in the chemistry of free radicals. The work of a number of authors (¹⁻³) has shown that diphenyl is formed from the phenyl radicals of benzoyl peroxide and benzene according to the equation:



But until now the question has not been touched upon at all of whether the free valence is retained at the carbon atom of the phenyl radical or whether isomerization may occur. O. A. Reutov (⁴), using C^{14} , discovered isomerization of the free *n*-propyl radical in solution. He showed that a reversible rearrangement process takes place:



V. V. Voevodskii and co-workers (⁵), using deuterated compounds, demonstrated rearrangement in alicyclic radicals.

In the present work, in order to detect possible isomerization of the phenyl radical, we used C^{14} -labeled BP with the label located in the benzene ring at the carbon bonded to the carboxyl. The synthesis of the labeled

Table 1

Reaction of benzoyl peroxide with benzene

BP, g	rel. activity of BP, imp/ml	benzene, ml	molar ratio BP/benzene	conversion, %	reaction rate, h	diphenyl, g	diphenyl, g	benzenol, g	$B_{\text{benz.}}$, mmol	B_{diphen} , mmol	Error, %
2.5	678	50	1 : 40	80	15	463	779	795	1.68		-2.1
2.5	678	50	1 : 40	80	18	465	735	800	1.58		-8.1
2.5	678	50	1 : 40	80	15	428	729	732	1.70		-0.4
3.0	678	60	1 : 50	80	15	416	738	715	1.77		+3.2
3.0	678	55	1 : 40	80	17	428	735	732	1.72		+0.4
3.0	678	60	1 : 50	80	15	422	689	725	1.63		-5.0

Table 2

Photodecomposition of benzoyl peroxide in benzene

BP, g	Specific activity of BP, imp/min	Benzene, ml	Molar ratio BP/benzene	Irradiation time, min	Diphenyl, g	Diphenyl, g	imp/min	Benzoic acid / Diphenyl	Error, %
5.0	678	80	1 : 40	100	232	392	398	1.69	-1.5
3.0	678	48	1 : 40	110	263	408	450	1.55	-9.3
3.0	678	48	1 : 40	117	207	326	352	1.58	-7.4

BP was carried out by the previously developed method ⁽⁶⁾. The results of the experiments are given in Table 1. Diphenyl was isolated from the reaction mixture by steam distillation and purified by repeated steam distillation (after purification, m.p. 70°; the mixed-melting-point test gave no depression); the yield was not determined, since special attention was paid to purification.

We had previously established that the formation of diphenyl during the photodecomposition of BP in benzene proceeds by a mechanism different from that in the thermal reaction; diphenyl is obtained only at the expense of BP:



i.e., the solvent does not take part in the reaction. Therefore it seemed of interest to us to investigate also the possibility of isomerization of the phenyl radical under these conditions.

The photodecomposition was carried out by irradiating solutions of BP in benzene (molar ratio 1 : 40) with a PRK-2 quartz lamp for 100-120 h at a temperature of 25-30°. The isolation and purification of diphenyl were carried out analogously to the thermal reaction (in the present case the diphenyl was diluted three- to fourfold with inactive diphenyl).

The results of the experiments are given in Table 2. Diphenyl was oxidized with chromic anhydride by the method ⁽⁸⁾. The benzoic acid obtained after oxidation was purified by sublimation (m.p. 121-122°); the mixed-melting-point test gave no depression. To detect possible isomerization of the phenyl radical, the relative activities of diphenyl and of the benzoic acid obtained by its oxidation were compared.

The relative activities were determined with an internal-filling counter with an accuracy of 3-4%, for which purpose the measured samples were burned by a micromethod to CO₂.

It may be assumed that isomerization is absent—hydrogen migration does not occur—or that isomerization proceeds with migration of a hydrogen atom into the meta position of the benzene ring (by analogy with the work of V. V. Vovodskii with the cyclohexyl radical ⁽⁵⁾ (a) and with migration of a hydrogen atom to any position of the benzene ring (6).

For convenience of discussion, let us introduce several conventional designations: *A* is the relative activity of a substance (imp/min) under the condition that all the activity is concentrated on one carbon atom in the molecule; *B* is the relative activity of a substance (imp/min), taking into account all carbon atoms in the molecule (the relative activity obtained from experiment); *n* is the number of carbon atoms in the molecule. According to the accepted notation,

$$B = \frac{A}{n}.$$

Let us consider the thermal reaction. If isomerization is absent, then phenyl radicals will add only at the position of the label:



In this case $A_{\text{diphen}} = A_{\text{benz. acid}}$, since all the activity of diphenyl passes into the acid.

$$B_{\text{diphen}} = A_{\text{diphen}}/12; \quad A_{\text{diphen}} = 12B_{\text{diphen}}.$$

$$B_{\text{benz. acid}} = A_{\text{benz. acid}}/7 = 12B_{\text{diphen}}/7; \quad B_{\text{benz. acid}}/B_{\text{diphen}} = 1.71.$$

In case (a), migration of the hydrogen atom takes place only to the meta position of the benzoyl ring:



where the label is distributed among three positions of the benzoyl ring, each with probability 1/3.

For this case:

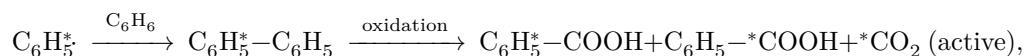
$$A_{\text{benz. acid}} = \frac{2}{3}A_{\text{diphen}}.$$

$$B_{\text{benz. acid}} = \frac{2}{3}A_{\text{diphen}}/7; \quad \text{but since } A_{\text{diphen}} = 12B_{\text{diphen}}, \quad B_{\text{benz. acid}} = 1.1B_{\text{diphen}}$$

and

$$B_{\text{benz. acid}}/B_{\text{diphen}} = 1.1.$$

For case (b), when migration of the hydrogen atom is possible to any position of the benzoyl ring, we obtain diphenyl with uniform distribution of the label over all six positions of the benzoyl ring:



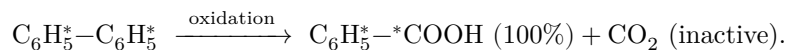
where the label is distributed over the six positions, each with probability 1/6.

And then $B_{\text{diphen}} = B_{\text{benz. acid}}$, since the label is uniformly distributed over all six atoms of the benzoyl ring, and

$$B_{\text{benz. acid}}/B_{\text{diphen}} = 1.$$

From six experiments on the thermal reaction of BP in benzene, the mean value of the ratios of the relative activities of benzoic acid to diphenyl is 1.68. This value is close to 1.71, i.e., to the case in which isomerization is absent. The deviation of the experimental value (1.68) from the calculated value (1.71) lies within the experimental error.

The arguments presented are also valid for the photodecomposition reaction of BP in benzene, with the sole difference that the absolute values of the relative activities are doubled, since in the diphenyl formed during photolysis both benzoyl rings are labeled:



In this case the relative activity of benzoic acid should be 1.71 times the relative activity of diphenyl. The mean value (obtained from three experiments on the photodecomposition of BP in benzene) of the ratios of the relative activities of benzoic acid to diphenyl is 1.64.

This figure is also close to 1.71, i.e., it characterizes the case of absence of isomerization in the phenyl radical. The deviation of the experimental value (1.64) from the calculated one (1.71) also lies at the limit of experimental error. On the basis of the data obtained, it may be stated that in the thermal reaction and photodecomposition of PB in benzene, isomerization of the phenyl radical does not occur. In addition, these results serve as experimental confirmation of the correctness of the synthesis of labeled PB ($\hat{6}$).

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

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