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Abstract

Full Text

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Effect of High Pressure on the Structural Orientation of the Phenylation of *tert*-Butylbenzene

(Presented by Academician B. A. Kazanskii, 15 IX 1962)

The role of steric hindrance in homolytic reactions is usually illustrated by the phenylation of alkylbenzenes with benzoyl peroxide ([1], [2]). Phenylation of *tert*-butylbenzene leads to the formation of a mixture of *tert*-butyldiphenyls containing only about 20% of the "hindered" 2-(ortho)-isomer ([3], [4]); at the same time, in the phenylation of toluene and ethylbenzene the content of the 2-isomer exceeds 50% ([3], [4]). The mechanism of the phenylation of alkylbenzenes has been studied in detail by many authors ([5]-[7]). At present it may be considered established that this reaction includes a slow stage of addition of the phenyl radical to the molecule of the aromatic hydrocarbon, with formation of a radical of type I:

$$\mathrm{ArH} + \mathrm{Ph}\cdot \rightarrow \left[\mathrm{Ar}\begin{matrix}\mathrm{Ph}\\ \\ \mathrm{H}\end{matrix}\right]\cdot$$

(I)

Radical I then eliminates a hydrogen atom as a result of interaction with another radical (for example, a benzoate radical) or with a molecule of benzoyl peroxide ([8]):

$$\left[\mathrm{Ar}\begin{matrix}\mathrm{Ph}\\ \\ \mathrm{H}\end{matrix}\right]\cdot + \mathrm{PhCOO}\cdot \rightarrow \mathrm{ArPh} + \mathrm{PhCOOH},$$

$$\left[\mathrm{Ar}\begin{matrix}\mathrm{Ph}\\ \\ \mathrm{H}\end{matrix}\right]\cdot + (\mathrm{PhCOO})_2 \rightarrow \mathrm{ArPh} + \mathrm{PhCOOH} + \mathrm{PhCOO}\cdot.$$

It has recently been found ([9]) that radicals of type I can also enter into reactions of dimerization and disproportionation with one another; in disproportionation, in particular, the same alkyldiphenyls are formed, as well as dihydroalkyldiphenyls. The fraction of alkyldiphenyls formed by this route is apparently small ([8]). Therefore, in the further discussion of the results of the

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study of the phenylation of *tert*-butylbenzene, we shall proceed from the assumption that the low content of the 2-isomer in the mixture of the resulting *tert*-butyldiphenyls is due to the steric hindrance of addition of the phenyl radical to the ortho position relative to the *tert*-butyl group of the alkylbenzene molecule. Then the ratio of the rate constants of the reactions of addition of phenyl radicals to the ortho, meta, and para positions is equal to the ratio of the contents of the corresponding isomers in the reaction products.

Let us now consider the question of the possible influence of pressure on the isomeric composition of the *tert*-butyldiphenyls formed. For this it is necessary to use the conclusions of transition-state theory. According to this theory ([10]), the change in the rate constant of the reaction (k) with increasing pressure (P) is determined by the equation

$$\left(\frac{\partial \ln k}{\partial P}\right)_T = -\frac{\Delta V^{\ddagger}}{RT}. \tag{1}$$

Here $\Delta V^{\neq}$ is the change in volume upon formation of one mole of the activated complex from the initial particles.

It was shown earlier ([11,12]) that in sterically hindered reactions the negative value of $\Delta V^{\neq}$ is greater than in analogous but sterically unhindered reactions. This leads to a greater acceleration of sterically hindered reactions with increasing pressure as compared with sterically unhindered ones.

Let the sterically unhindered phenylation of tert.-butylbenzene with formation of 4-(para)-tert.-butyldiphenyl be characterized by the activation volume effect $\Delta V_4^{\neq}$, while the sterically hindered formation of the transition state in 2-substitution is accompanied by a decrease in volume $\Delta V_2^{\neq}$. From what has been said above it follows that the absolute negative value of $\Delta V_2^{\neq}$ is greater than the value of $\Delta V_4^{\neq}$ by an amount $\Delta\Delta V^{\neq}$, which characterizes the steric hindrance of ortho-substitution as compared with para-substitution (see ([12])).

Table 1

Phenylation of tert.-butylbenzene in various apparatus at 80°

No. of experiments	P	τ, h	2-isomer	3-isomer	4-isomer
			Composition of tert.-butyldiphenyls, %	Composition of tert.-butyldiphenyls, %	Composition of tert.-butyldiphenyls, %
	In glass				

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No. of experiments	P	τ, h	2-isomer	3-isomer	4-isomer
1	Atmospheric	72	16.7	53.5	29.8
2	Atmospheric	40	16.5	54.2	29.3
2	Atmospheric	77	16.4	53.5	30.1
	In a steel reactor				
3	Atmospheric	8	17.0	52.1	30.9
3	Atmospheric	16	16.6	52.6	30.8
3	Atmospheric	48	16.3	52.5	31.2
3	Atmospheric	72	16.8	52.8	30.4
4	2000 kg/cm^2	72	23.1	49.7	27.2
	In a lead ampoule				
5*	Atmospheric	40	19.6	50.9	29.5
5*	Atmospheric	77	19.3	50.7	30.0
6*	Atmospheric	6	19.0	51.8	29.2
6*	Atmospheric	16	19.3	50.6	30.1
6*	Atmospheric	40	19.6	50.7	29.7
6*	Atmospheric	72	18.8	51.4	29.8
	Average		19.3	51.0	29.7
7	2000 kg/cm^2	8	25.2	48.0	26.8
8	2000 kg/cm^2	8	25.4	48.4	26.2
9	4000 kg/cm^2	8	28.3	46.3	25.4
10	4003 kg/cm^2	8	27.8	46.8	25.4
11	6000 kg/cm^2	8	29.8	46.1	24.1
12	6000 kg/cm^2	8	29.8	46.2	24.0

* The experiment was carried out in a glass vessel with lead plates.

In accordance with equation (1), one may expect that, in the phenylation of tert.-butylbenzene, increasing the pressure will lead to an increase in the content of the most "hindered" (i.e., ortho-) isomer in the reaction products. The present work was devoted to testing this assumption.

Experimental part

Experiments on the phenylation of tert.-butylbenzene with benzoyl peroxide at atmospheric pressure were carried out with the same amounts of starting substances (8 g of benzoyl peroxide, 155 ml of tert.-butylbenzene) and at the same temperature (80°) as in the work of Cadogan, Hey, and Williams (3). Analysis of the mixture of tert.-butyldiphenyls was carried out not by a spectral method, as in (3), but by gas-liquid chromatography on an SKB IOKh chromatograph (after washing out the esters and removing acids from the reaction mixture). Good separation of the isomeric tert.-butyldiphenyls was achieved on a 2-meter column (*d*-5 mm) with polyethylene glycol adipinate (15%) on diatomaceous brick at 170°. Helium (50 ml/min) was used as the carrier gas.

The experiments were conducted both in glass and in steel* apparatus. The total yield of tert.-butyldiphenyls in our experiments at atmospheric pressure (42.6 wt.% relative to the initial benzoyl peroxide) was close to that obtained in work (3) (46.5 wt.%); however, the content of the 2-isomer proved to be somewhat lower (about 17%) than in the cited work (24%). It is possible that the overestimated yield of the 2-isomer in (3) is explained by the presence in the high-boiling residue (after distillation of the mixture of tert-butyldiphenyls) of some amount of the 3- and 4-isomers, which remained unaccounted for in the spectral analysis.

The use of gas–liquid chromatography made it possible for us to determine the content of the various isomers in the mixture of tert-butyldiphenyls during the reaction (see Table 1).

The data presented in Table 1 show that in glass and steel apparatus the content of the various isomers is identical and remains constant during the reaction. Consequently, the tert-butyldiphenyls formed do not enter into secondary reactions that could affect the relative content of one or another isomer in their mixture.

We carried out an experiment in a steel reactor at a pressure of 2000 kg/cm^2. The results of this experiment, also given in Table 1, indicate a noticeable increase in the content of the 2-isomer in the mixture of tert-butyldiphenyls formed; this increase substantially exceeds the deviations in the results of the analysis of parallel experiments at atmospheric pressure.

Table 2

Effect of pressure on the ratio of tert-butyldiphenyls

Reactor material	Pressure	2 : (3+4)	2 : 4	3 : 4
Steel	Atmospheric	0.202	0.550	1.73
Steel	2000 kg/cm^2	0.300	0.848	1.83

* The steel reactor used is described in work (13).

Reactor material	Pressure	2 : (3+4)	2 : 4	3 : 4
Lead	Atmospheric	0.239	0.650	1.72
Lead	2000 kg/cm^2	0.338	0.955	1.82
Lead	4000 kg/cm^2	0.390	1.105	1.83
Lead	6000 kg/cm^2	0.425	1.24	1.91

To carry out experiments at still higher pressures, we used a multiplier (14), into which lead ampoules (capacity 5 ml) were placed; these contained a solution of benzoyl peroxide in tert-butylbenzene in the same ratio as in the preceding experiments. Preliminary experiments were carried out to determine whether the presence of lead affects the ratio of the resulting isomeric tert-butyldiphenyls at atmospheric pressure. For this purpose, lead plates were placed in glass flasks with the reaction mixture in such a way that they filled a considerable part of the flask volume. The results of these experiments, as well as of experiments in lead ampoules at higher pressures, are summarized in Table 1.

The data given in Table 1 indicate that the presence of lead affects the isomer ratio of interest to us; the fraction of 2-tert-butyldiphenyl in the experiments at atmospheric pressure is about 19%, i.e., 2% greater than in glass or steel apparatus (this difference exceeds the error of the analysis). At a pressure of 2000 kg/cm^2, the fraction of the 2-isomer also proved to be 2% higher than in steel apparatus. Raising the pressure to 4000 kg/cm^2 led to a further increase in the fraction of this "hindered" isomer, which already amounted to 28%. At a pressure of 6000 kg/cm^2, the content of the 2-isomer rose to 30%.

Discussion of the Results

The data obtained in the present work on the effect of pressure on the ratio of isomeric tert-butyldiphenyls are summarized in Table 2.

From the data given in Table 2 the following conclusions can be drawn:

1. The ratio of the content of the 2-isomer to the sum of the other two isomers increases significantly with increasing pressure. Increasing the pressure from atmospheric to 6000 kg/cm^2 leads to an increase in this ratio by more than 70%.
2. The ratio changes most substantially with increasing pressure

2- and 4- (i.e., the most "hindered" and "unhindered") isomers: it increases (in lead) from 0.65 at atmospheric pressure to 1.24 at a pressure of 6000 kg/cm^2, i.e., almost twofold. 3. The ratio of the contents of the 3-isomer and 4-isomer increases only slightly with increasing pressure.

Thus, the results of the present work show the possibility of influencing the structural direction of chemical reactions by means of high pressure, as a result of preferential acceleration of the reaction in the direction that is most sterically hindered.

According to the assumption stated above (see p. 105), the fraction of a given isomer in the mixture of tert-butyldiphenyls is proportional to the rate constant for addition of the phenyl radical to the corresponding carbon atom of the ring in the tert-butylbenzene molecule. The change in the ratio of the 2- and 4-isomers with increasing pressure makes it possible to calculate the value of $\Delta\Delta V^{\neq}$ from equation (1):

$$\frac{\partial \ln\left(\frac{[2]}{[4]}\right)}{\partial P} = -\frac{\Delta\Delta V^{\neq}}{RT}, \tag{2}$$

where [2] and [4] are the concentrations of 2- and 4-tert-butyldiphenyls.

Graphical differentiation of the curve $\ln([2]/[4]) - P$ gives a value of $\Delta\Delta V^{\neq}$ equal to approximately 5 cm^3/mol at atmospheric pressure.

In conclusion, we note that in the present work a slight influence of lead on the composition of the isomers was observed (but one still exceeding the limits of experimental error); the causes of this phenomenon require further investigation.

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