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Abstract

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DECOMPOSITION OF DIPHENYLMERCURY IN CYCLOHEXANE AND CYCLOHEXENE

In one of our previous works ([1]) we showed that the decomposition of diphenylmercury in benzene proceeds with the participation of the latter according to the overall equation

$$(^{14}C_6H_5)_2Hg + C_6H_6 \rightarrow {}^{14}C_6H_5 - C_6H_5 + {}^{14}C_6H_6 + Hg. \quad (1)$$

It was assumed that the process proceeds homolytically in the reaction complex. For the study of free-radical reactions it would be interesting to determine how diphenylmercury decomposes in nonaromatic solvents. As such solvents we chose cyclohexane and cyclohexene. Experiments were carried out on both the photodecomposition and the thermal decomposition of this compound.

Photodecomposition of $(C_6H_5)_2Hg$ was carried out in quartz ampoules by irradiating the reaction mixture with a PRK-7 mercury lamp. The reaction was conducted in vacuum and with access of air. Evacuation of the ampoules was performed by threefold freezing (thawing) of their contents, with a corresponding number of air-pumping operations. The ampoules evacuated in this way were sealed, while the ampoules in which the reaction was conducted in the presence of air were closed with a cork stopper. The weighed portions of diphenylmercury in the various experiments were about 10–15 g; the molar ratio of the starting substances was maintained constant ($(C_6H_5)_2Hg : C_6H_{12} = 1 : 30$). Upon irradiation of the ampoules with ultraviolet light for 100–150 h, decomposition amounted to 60–90%. The extent of decomposition was determined from the amount of metallic mercury precipitated.

Table 1

Photodecomposition of diphenylmercury* in cyclohexane
$(C_6H_5)_2Hg$ (mol.) : C_6H_{12} (mol.) $= 1 : 30$

Reaction products	Vacuum, experiment No. 1	Vacuum, experiment No. 2	Air atmosphere, experiment No. 3	Air atmosphere, experiment No. 4
In cyclohexane $(C_6H_5)_2Hg$ (mol.) : C_6H_{12} (mol.) = 1 : 30				
Benzene	150.3	159.9	162	163.6
Dicyclohexyl	46.9	45.8	27.9	38.0
Cyclohexene	30.1	32.9	32.8	22.16
Phenylcyclohexane	2.5	5.7	7.2	3.5
Diphenyl	4.1	3.8	11.5	6.3
In cyclohexene $(C_6H_5)_2Hg$ (mol.) : C_6H_{10} (mol.) = 1 : 30				
Benzene	157	152		
Dicyclohexenyl	70	74		

* The number of moles of mercury liberated, as well as the amount of diphenylmercury decomposed, is taken as 100%.

The experiments showed (Table 1) that during the photodecomposition of diphenylmercury in cyclohexane, mercury, benzene, dicyclohexyl, cyclohexene, and small amounts of biphenyl and phenylcyclohexane are formed. In the case of the reaction in an air atmosphere, cyclohexanol and cyclohexanone are also obtained. In the decomposition of $(C_6H_5)_2Hg$ in cyclohexene, mercury, benzene, and dicyclohexenyl were found (Table 1).

As can be seen from the table, in the photodecomposition of diphenylmercury in cyclohexane and cyclohexene, the phenyl radicals of the organometallic compound are converted predominantly into benzene (75–80%). In contrast to the reaction with benzene, which proceeds in the reaction cage ([1]), the reactions of diphenylmercury with cyclohexane and cyclohexene proceed by a free-radical mechanism. The phenyl radicals formed upon dissociation of the organomercury compound abstract hydrogen from the solvent, regenerating secondary radicals:

$$C_6H_5^{\bullet} + C_6H_{12} \leftarrow C_6H_6 + C_6H_{11}^{\bullet}, \qquad (2)$$

$$C_6H_5^{\bullet} + C_6H_{10} \rightarrow C_6H_6 + C_6H_9^{\bullet}. \quad (3)$$

The latter may dimerize, disproportionate, and interact with other radicals.

In the case of cyclohexene there are two possible paths for the formation of benzene: from the phenyl rings of diphenylmercury, and through deep dehydrogenation of the solvent by phenyl radicals. To clarify this supposition, we carried out experiments on the photo- and thermodecomposition of ^{14}C-labeled diphenylmercury in pure cyclohexene. It turned out that the isotopic composition of the benzene obtained as a result of the reactions is the same as that of the starting diphenylmercury. This indicates that dehydrogenation of cyclohexene with abstraction of four hydrogen atoms does not occur. Benzene is formed only from the radicals of the organomercury compound. In our opinion, hydrogen abstraction from cyclohexene proceeds predominantly from the α-carbon atoms. The isolated dicyclohexenyl probably contains isolated double bonds. There are indications in the literature ([2]) that the reaction of peroxides with cyclohexene is accompanied by dehydrodimerization of the latter; in this case hydrogen abstraction from the solvent proceeds predominantly from the allylic position.

In addition, it should be noted that the decomposition reaction of $(C_6H_5)_2Hg$ in cyclohexene is significantly accelerated by peroxide compounds, which, as is known ([3]), can readily form during storage of cyclohexene in air. Therefore, in the work we used cyclohexene freshly distilled over sodium in a nitrogen atmosphere.

As can be seen from Table 1, during the photodecomposition of diphenylmercury in cyclohexane in an air atmosphere, considerably less dicyclohexyl and cyclohexene is obtained than in vacuum. Probably, the cyclohexyl radicals are oxidized by atmospheric oxygen to cyclohexanone and cyclohexanol, the presence of which in the reaction mixture was demonstrated by us.

The reactions of the thermodecomposition of diphenylmercury in cyclohexane were carried out in glass ampoules at 260-280°. At these temperatures it did not seem possible to conduct the reaction with large quantities of substances. Therefore, no more than 2-3 g of the organomercury compound was taken, and the molar ratio of the starting substances was maintained the same as in the photodecomposition. In most experiments the extent of reaction after 50 h of heating did not exceed 15-20%. At 260° over 150 h the reaction proceeded to 8.7%. In this case, mercury, benzene, cyclohexene, phenylcyclohexane, and traces of biphenyl were found. We were unable to detect dicyclohexyl in the reaction mixture. In contrast to photo-thermodecomposition, the thermodecomposition is accompanied by the separation of a considerable amount of a sparingly soluble polymeric compound $(-C_6H_4-Hg-)_n$, whose formation we had also observed earlier in reactions of diphenylmercury with other solvents.

Analysis of the reaction products was carried out on an IKS-14 infrared spec-

trophotometer in the frequency range 400–2000 cm^{-1}. For the quantitative determination of the components, a calibration plot was constructed in the coordinates: optical density (D)—concentration (C, %). Benzene and cyclohexene were determined quantitatively in the solution of cyclohexane distilled off after the reaction, at the analytical frequencies 1820 cm^{-1} and 720 mm^{-1}. The remaining reaction products, after steam distillation, were dissolved in carbon tetrachloride. The content of dicyclohexyl, diphenyl, and phenylcyclohexane in the solution was determined from absorption bands with frequencies of 600, 545, and 525 cm^{-1}, respectively. In the case of the reaction in cyclohexene, benzene was determined quantitatively by the isotope dilution method. A weighed portion of benzene labeled with C^{14} and of known activity was introduced into the reaction mixture. After mixing, it was isolated as m-dinitrobenzene and analyzed for C^{14} content. Dicyclohexenyl was isolated from the reaction mixture by steam distillation. After distillation in vacuo it was analyzed for molecular weight, elemental composition, and double bonds.

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