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Abstract

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Study of the Reaction of Organic Compounds of Mercury and Lead by Isotopic and Mass-Spectrometric Methods

Earlier we showed ([1,2]) that in the photo- and thermal decomposition of diphenylmercury, tetraphenyllead, and hexaphenyldilead in benzene, the principal reaction product is biphenyl. With the aid of substances labeled with C^{14}, it was shown that the biphenyl formed in this process contains phenyl groups of the benzene solvent. We represented the process of decomposition of diphenylmercury in benzene by the following overall equation:

$$(C_6H_5)_2Hg + C_6^*H_6 \rightarrow [(C_6H_5)_2Hg \cdot C_6^*H_6] \xrightarrow{h\nu} C_6H_5C_6^*H_5 + C_6H_6 + Hg \quad (1)$$

As is seen from the equation, 50% of the phenyl rings in biphenyl should come from benzene. In reality, however, the amount of the latter was always less than that indicated and varied on average from 42 to 48%. From this it followed that in this reaction biphenyls of another composition are also formed, the presence of which leads to a change in the radioactivity of the isolated products.

Table 1

Decomposition of diphenylmercury in benzene

Isotopic forms	initial benzene	Content of isotopic varieties of benzene, % after photodecomposition of $(C_6H_5)_2Hg$, experiment 1	Content of isotopic varieties of benzene, % after thermodecomposition of $(C_6H_5)_2Hg$, experiment 2	Content of isotopic varieties of benzene, % after photodecomposition of $(C_6D_5)_2Hg$, experiment 3*
C_6H_6	–	0.09**	0.46	99.5
C_6H_5D	–	0.14	0.10	–
$C_6H_4D_2$	0.05	0.06	0.04	–
$C_6H_3D_3$	0.40	0.41	0.43	0.01

Isotopic forms	initial benzene	Content of isotopic varieties of benzene, % after photodecomposition of $(C_6H_5)_2Hg$, experiment 1	Content of isotopic varieties of benzene, % after thermodecomposition of $(C_6H_5)_2Hg$, experiment 2	Content of isotopic varieties of benzene, % after photodecomposition of $(C_6D_5)_2Hg$, experiment 3*
$C_6H_2D_4$	3.80	3.90	3.86	0.04
C_6HD_5	24.0	22.3	24.8	0.34
C_6D_6	71.6	73.3	70.4	0.09
Yield, %	94.4	94.7	94.0	0.4

* In experiment 3 benzene was used.
** The relative error in measuring the content of benzenes (biphenyls) did not exceed 3%.

It could be assumed that, upon decomposition of diphenylmercury in labeled benzene, three possible isotopic varieties of biphenyl might be obtained: A—$C_6H_5C_6^*H_5$, B—$C_6H_5C_6H_5$, C—$C_6^*H_5C_6^*H_5$.

The C^{14} method, used by us in previous studies, gave an idea only of the total content of label in biphenyl; therefore it was impossible to establish its composition by means of radiocarbon. The ratio of biphenyls A, B, and C to one another is readily determined by mass-spectrometric analysis using one of the components labeled with deuterium ([3]).

In the present work we carried out a series of experiments on the photo- and thermal decomposition of diphenylmercury, tetraphenyllead, and hexaphenyldilead in completely deuterated benzene C_6D_6, as well as of deuterated organometallic compounds (MOC) $(C_6D_5)_2Hg$, $(C_6D_5)_4Pb$ in ordinary benzene. The ratio of MOC to solvent was taken from 1 : 100 to 1 : 500 moles. Photoreactions were carried out in evacuated quartz ampoules. The reaction mixture was irradiated with a PRK-7 lamp. Thermal reactions were conducted in ampoules made of thick-walled glass, likewise in the absence of air. After the reaction the ampoules were opened in air. The benzene solvent was distilled off on a small column. Biphenyl was distilled off with steam. The material not decomposed during the reaction

OMC were recrystallized from benzene and, in the dry state, subjected to catalytic decomposition on platinum black with liberation of diphenyl.

The diphenyls obtained in this way, as well as the benzene after the reaction, were analyzed for isotopic composition by low-voltage mass spectrometry [4,5]. Examples of analyses are given in Tables 1 and 2.

It was found that the photochemical and thermal decomposition of diphenylmercury, tetraphenyltin, and hexaphenyldiplumbane in benzene C_6D_6 is accompanied by the appearance, in the solvent, of benzene molecules C_6H_6 and C_6H_5D, which were not present in the initial benzene. At the same time, diphenyl of all three varieties (A, B, C) was found in the reaction products.

The same data were obtained in experiments in which deuterated OMC, $(C_6D_5)_2Hg$, $(C_6D_5)_4Pb$, and ordinary benzene were taken. Here the appearance of benzene molecules C_6D_5H, $C_6D_4H_2$, $C_6D_3H_3$, as well as all three isotopic forms of diphenyls, was observed.

We believe that the decomposition of the indicated OMC in benzene proceeds by a homolytic type. The mechanism of these transformations will be considered in somewhat greater detail using diphenylmercury as an example.

Table 2

Decomposition of diphenylmercury in benzene

Isotopic form of diphenyl	Experiment 1 I	Experiment 1 II	Experiment 2 I	Experiment 2 II	Experiment 3 I	Experiment 3 II	Experiment 3 III
$C_{12}H_{10}$	7.6	89.2	64.8	59.0	1.2	0.13	0.13
$C_{12}H_9D$	0.41	9.8	3.0	2.3	0.03	0.01	0.04
$C_{12}H_8D_2$	0.39	0.4	0.3	0.1	0.08	0.03	–
$C_{12}H_7D_3$	2.60	0.2	0.9	1.4	0.57	0.06	–
$C_{12}H_6D_4$	18.9	0.1	6.5	8.6	2.88	0.54	0.06
$C_{12}H_5D_5$	65.0	0.2	20.9	23.4	80.6	2.66	0.31
$C_{12}H_4D_6$	0.18	0.3	0.4	–	0.18	0.84	0.11
$C_{12}H_3D_7$	0.10	0.1	0.1	–	0.06	0.64	0.16
$C_{12}H_2D_8$	1.11	–	0.4	2.1	0.60	4.70	2.18
$C_{12}HD_9$	2.80	–	1.2	3.0	2.52	20.6	18.4
$C_{12}D_{10}$	0.91	–	2.4	0.1	4.39	69.8	78.4
Degree of deuteration, %	44.5	1.6	17.8	20.7	51.7	94.6	96.7

Notes: The experiment numbers correspond to Table 1.
I –diphenyl obtained as a result of the decomposition of diphenylmercury in benzene.
II –diphenyl obtained by decomposition of the remaining diphenylmercury on Pt.
III –diphenyl obtained by decomposition of the initial diphenylmercury on Pt.

In the photoreaction between diphenylmercury (0.00530 mole) and C_6D_6 (taken in a molar ratio of 1 : 100), after 500 h of irradiation there were isolated 0.00172 mole of metallic mercury, 0.00173 mole of diphenyl, and 0.0013 mole of the new forms of benzene C_6H_6 and C_6H_5D. On the basis of these and the mass-spectrometric data (see experiment 1), it was calculated that the isolated diphenyl consisted of: unlabeled diphenyl B –0.00013 mole (7.6% of all diphenyl), half-labeled diphenyl A (isotopic forms from $C_{12}D_5H_5$ to $C_{12}DH_9$) –0.00152 mole (88%), and completely labeled diphenyl C, with isotopic forms from $C_{12}D_{10}$ to $C_{12}D_6H_4$ –0.00008 mole (5%). The benzene solvent was enriched in the forms C_6H_6 –0.00005 mole (39%) and C_6H_5D –0.0008 mole (61% of the benzene formed from diphenylmercury).

The results presented undoubtedly indicate that, in this reaction, the OMC radicals react by different pathways. The formation of unlabeled diphenyl, consisting entirely of diphenylmercury radicals, is well explained by the occurrence of intramolecular decomposition of some fraction of $(C_6H_5)_2Hg$, in which the benzene solvent does not participate.

$$(C_6H_5)_2Hg \rightarrow C_6H_5C_6H_5 + Hg \quad (2)$$

It is known that such processes are catalyzed by metals [(6)]. Therefore the reaction may be represented as the catalytic decomposition of $(C_6H_5)_2Hg$ with recombination of radicals on the metal surface.

As already noted, the principal isotopic form of diphenyl in the photolysis reaction of diphenylmercury is half-labeled diphenyl –A. The formation of this product may partly be explained by reaction 1, in which, it seems to us, redistribution of the valence bonds occurs in the reacti-

complex. In addition to diphenyl, in reaction (1) benzene of the form C_6H_5D is isolated. Its content should be equivalent to the amount of $C_6H_5^*C_6H_5$. In reality, however, there is always less C_6H_5D benzene than calculated. But alongside C_6H_5D benzene, C_6H_6 benzene was found, amounting to as much as 39% of their total. Yet even taking this form of benzene into account, their content does not reach the number of moles of the diphenyl A obtained. It follows from this that the formation of the products under consideration, $C_6H_5^*C_6H_5$ and C_6H_6, proceeds also by other pathways. One such pathway may be the decomposition of diphenylmercury ([7]) into the radicals $C_6H_5\cdot$ and $C_6H_5Hg\cdot$. The latter, in photoreactions, also dissociates almost completely into $C_6H_5\cdot$ and Hg. In our opinion, the $C_6H_5\cdot$ radicals formed in a medium of aromatic solvents are immediately bound into unstable π-complexes, which we shall denote $(C_6H_5\cdot)^*$. Subsequently, according to the scheme of homolytic arylation accepted by many authors ([9]), such radicals are transformed into dihydrodiphenyl radicals $C_6H_5C_6D_5D\cdot$, with subsequent transfer of deuterium (hydrogen) to acceptor radicals $(C_6H_5\cdot)$ and to σ-radicals $C_6H_5C_6D_5D$.

In the first case this results in the formation of C_6H_5D (partly ** C_6H_6); in the second, diphenyl A and dihydrodiphenyl are also formed. An additional amount of diphenyl A may be obtained through oxidation by atmospheric oxygen of dihydrodiphenyl during the isolation of the products formed. Such a picture was observed earlier ([10]) in the decomposition of benzoyl peroxide in deuteriobenzene. This may explain why somewhat more diphenyl A is obtained than benzene of the forms C_6H_5D and C_6H_6. However, this question requires further investigation.

The existence among the products of the third type of reaction of diphenyl —diphenyl B—once again testifies to the participation of free radicals in the decomposition of diphenylmercury. Diphenyl of this form could have been obtained in the presence of exchange of the MOC with the solvent. We observed such exchange for diphenylmercury during its thermal decomposition. In photoreactions there is almost no exchange, since very little deuterium was present in the diphenylmercury isolated after the reaction (1.6%; see experiment 1).

At present we still do not know the details of the mechanism of formation of phenyl radicals from the solvent, nor the pathways by which diphenyl B is formed from them. However, there is no doubt that its presence in the products formed is connected with the passage of phenyl radicals through benzene (chain-transfer reaction). For clarity, we depict these processes as follows:

$$C_6H_5\cdot + C_6D_6 \rightarrow C_6H_5D + C_6D_5\cdot \quad (3)$$

$$C_6D_5\cdot + C_6D_6 \xrightarrow{[-D]} C_6D_5C_6D_5. \quad (4)$$

In order to confirm the data presented above, we investigated the photodecomposition of labeled diphenylmercury $(C_6D_5)_2Hg$ in ordinary benzene (experiment 3). Here, too, the appearance of all three isotopic diaryl forms, A, B, and V, was noted. In the benzene solvent after the reaction, new benzene forms from C_6D_6 to $C_6D_3H_3$ were found.

These results fully confirm the conclusions made above. In addition, it was possible to establish the source of formation of the benzenes C_6H_6 and C_6D_6. In the first experiments it might still have been assumed that the appearance of C_6H_6 benzene was connected with an isotope effect, i.e., with preferential abstraction of hydrogen, rather than deuterium, by phenyl radicals from the benzene solvent. In the experiment in which $(C_6D_5)_2Hg$ and ordinary benzene were taken, as a result of which the isotope effect was excluded, formation of C_6D_6 benzene was observed. Consequently, in the process of decomposition of diphenylmercury, radicals abstract hydrogen not only from the solvent but also from radicals.

* In some works ([8]) they were denoted as $C_6H_5\cdot(C_6H_6)$.

** The initial benzene solvent in these experiments contained from 6 to 10% hydrogen atoms.

diphenylmercury. It is possible that this is connected with the fact that the reaction products always contain infusible organometallic compounds of condensed structure.

Photolysis of tetraphenyllead and hexaphenyldilead in C_6D_6, as well as of labeled tetraphenyllead $(C_6D_5)_4Pb$ in ordinary benzene, gives exactly the same products as in the reaction with diphenylmercury. Thus, for example, photoirradiation of tetraphenyllead in C_6D_6 (taken in a molar ratio of 1 : 250) for 200 hours led to the formation of biphenyl, in which biphenyl A—94.7%, biphenyl B—4.3%, and biphenyl C—0.7% were found. In the composition of the benzene after the reaction we found 0.12% benzene C_6H_6 and 0.02% benzene C_6H_5D. The $(C_6H_5)_4Pb$ that had not decomposed in the reaction contained only 0.2% deuterium.

The results of experiments on the photodecomposition of $(C_6D_5)_4Pb$ in ordinary benzene are analogous to the results with diphenylmercury.

In the photodecomposition of hexaphenyldilead in C_6D_6 (molar ratio 1 : 200, irradiation time 200 hours), biphenyl was obtained that consisted of biphenyl A—94.4%, biphenyl B—7.6%, and biphenyl C—1.6%. In the composition of the benzene isolated from the reaction, C_6H_6—0.27% and C_6H_5D—0.08% were present. In the hexaphenyldilead that had not decomposed after irradiation, less than 0.02% deuterium was detected.

In the thermal reaction of diphenylmercury in C_6D_6 (ratio of components 1 : 100, temperature 290-300°, heating time 11 h), the formation of a large amount of biphenyl B is observed (experiment 2), which indicates that under these conditions the decomposition of $(C_6H_5)_2Hg$ proceeds predominantly according to scheme 2. In addition, under the conditions of thermal decomposition diphenylmercury exchanges phenyl radicals with benzene. We had also previously observed the exchangeability of diphenylmercury [1] with the aid of C^{14}.

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CITED LITERATURE

1. G. A. Razuvaev, G. G. Petukhov, Yu. A. Kaplin, DAN, **135**, 342 (1960).
2. G. A. Razuvaev, G. G. Petukhov, Yu. A. Kaplin, ZhOKh, **33**, 2404 (1963).
3. I. P. Gragerov, M. Ya. Turkina, DAN, **140**, 1317 (1961).
4. G. A. Semenov, M. Ya. Turkina, Zav. lab., **24**, 1084 (1958).
5. G. A. Semenov, M. Ya. Turkina, V. V. Troshin, V. I. Karpunin, Collection of Papers of the State Institute of Applied Chemistry, issue 45, L., 1960, p. 133.

6. G. A. Razuvaev, M. M. Koton, ZhOKh, **3**, 792 (1933); G. A. Razuvaev, G. G. Petukhov, B. G. Zateev, DAN, **127**, 348 (1959).

7. G. A. Razuvaev, G. G. Petukhov, A. F. Rekasheva, G. P. Miklyukhin, DAN, **90**, 569 (1953).

8. G. G. Petukhov, Usp. khimii, **30**, 1433 (1961).

9. R. I. Milyutinskaya, Kh. S. Bagdasaryan, E. A. Izrailevich, ZhOKh, **31**, 1019 (1957).

10. E. L. Eliel, S. Meyerson, Z. Welvart, S. H. Wilen, J. Am. Chem. Soc., **82**, 2936 (1960).

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