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Abstract

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REACTIONS OF DIPHENYLMERCURY WITH BENZENE

In a number of works we have carried out studies of numerous reactions of diphenylmercury in various solvents, which proceed upon heating or under the action of ultraviolet light ([1]). Most of the processes studied proceed by a free-radical mechanism through dissociation of the C_6H_5—Hg bond. In one of the works, in which labeled organomercury compounds were used, it was observed that the photodecomposition of diphenylmercury in benzene is accompanied by a slight exchange of benzene rings ([2]):

$$(C_6H_5)_2Hg + C_6D_6 \rightleftharpoons C_6H_6 + (C_6D_5)_2Hg.$$

Later I. A. Korshunov and A. A. Orlova ([3]) confirmed the presence of this process (3-10%) in photothermal reactions of diphenylmercury in labeled C^{14} benzene, which they explain by reversibility of the dissociation reaction of $(C_6H_5)_2Hg$. In both cases they conducted the reactions in ampoules not evacuated of air.

All experiments previously carried out by us were also performed in the presence of air.

The exceptionally strong action of oxygen on the decomposition of $(C_6H_{11})_2Hg$, as well as the considerable effect, discovered by us, of oxygen on the isotopic composition of diphenyl obtained in the thermal decomposition of tetraphenyllead in labeled C^{14} benzene, prompted us to carry out a more detailed investigation of the role of oxygen in reactions with diphenylmercury.

For this purpose experiments were set up on the decomposition of ordinary diphenylmercury in a solution of $C^{14}H_6$, and conversely—of C^{14}-labeled diphenylmercury in ordinary benzene. The experiments were carried out both in an evacuated system and in the presence of air or pure oxygen. Evacuation of the ampoules was carried out by triple freezing (thawing) of the reaction mixture with the appropriate number of operations for pumping out the air. The decomposition process was induced by the action of temperature or by irradiation with a PRK-7 quartz lamp. The photodecomposition experiments were carried out in quartz ampoules identical in diameter and wall thickness.

Upon heating ordinary diphenylmercury in labeled C^{14} benzene to 260° in vacuum and in the presence of oxygen, two processes are observed: 1) decomposition of $(C_6H_5)_2Hg$ into mercury, diphenyl, and a small amount of resinous substances; 2) exchange of C_6H_5 radicals between benzene and diphenylmercury. In vacuum both processes proceed extremely slowly (Table 1), and the exchange reaction is observed even before appreciable decomposition of diphenylmercury (experiment 1) and increases in the course of its decomposition. Thus, when the reaction mixture is heated in vacuum for 190 hours, the exchange reaches 13.9%, whereas decomposition proceeds only to 2.7% (experiment 2).

In the presence of air the rates of both processes increase sharply and subsequently again become insignificant (Table 1, experiments 3 and 4). This effect is expressed still more sharply when the ampoule is filled with pure oxygen (experiment 5).

It turned out that the diphenyl formed during thermal decomposition in vacuum consists to the extent of 40% of the phenyl rings of benzene—the solvent. The isotopic composition of the diphenyl obtained in an analogous reaction in an oxygen atmosphere reaches 63% of the initial activity of the benzene. This composition of diphenyl is explained by the fact that the thermal decomposition of diphenylmercury in the presence of oxygen is accompanied by a reaction of exchange of radicals of the mercury compound with the solvent. As is seen from Table 1, the latter process under these conditions reaches a considerable magnitude. Therefore, in this case it is very difficult to judge the mechanism of decomposition of $(C_6H_5)_2Hg$ from the composition of the diphenyl.

Table 1

Thermal decomposition of diphenylmercury in radioactive benzene $(C_6H_5)_2Hg$ (mol.) : $C_6^*H_6$ (mol.) $= 1 : 15,\ t = 260°$

No. of experiment	Experimental conditions	$(C_6H_5)_2Hg$, g	Benzene, g	Benzene, act., imp./min	Heating duration, h	Extent of decomposition, %	Activity of isolated $(C_6H_5)_2Hg$, imp./min	Extent of exchange, %
1	Vacuum	1.8	6.16	3455	14	0	52	1.5
2	»	3.6	12.32	1890	190	2.7	263	13.9
3	Air atmosphere	0.9	3.08	3455	14	19.2	446	12.9
4	Same	1.8	6.16	3455	33	16.4	557	16.1

No. of experiment	Experimental conditions	$(C_6H_5)_2Hg$, g	Benzene, g	Benzene, act., imp./min	Heating duration, h	Extent of decomposition, %	Activity of isolated $(C_6H_5)_2Hg$, imp./min	Extent of exchange, %
5	Oxygen atmosphere	1.8	6.16	3455	14	40.7	1080	31.2

Notes. 1. The extent of decomposition was determined from the amount of mercury precipitated.
2. The extent of exchange is determined as the ratio of the activity of diphenylmercury to the initial activity of benzene.

Thus, the processes occurring upon heating diphenylmercury in benzene solution in the presence of O_2 are very complex. In the present communication some preliminary data are presented, still insufficient for their complete analysis.

Table 2

Dependence of the extent of thermal decomposition of diphenylmercury in labeled benzene on the amount of oxygen present in the ampoule.
$(C_6H_5)_2Hg$ (mol.) : $C_6^*H_6$ (mol.) $= 1 : 15$; $t = 260°$.
Heating duration 14 h.

No. of experiment	$\frac{O_2 \text{ (mol)}}{(C_6H_5)_2Hg \text{ (mol)}}$	Initial benzene activity, imp./min	Extent of decomposition, %	Activity of $(C_6H_5)_2Hg$ after reaction, imp./min	Extent of exchange, %	$\frac{Hg \text{ (mol)}}{O_2 \text{ (mol)}}$
1	0.000	2000	0	34	1.7	–
2	0.016	1700	21.6	233	13.7	13.5
3	0.068	1700	32.7	457	26.9	4.8
4	0.107	1700	48.7	576	33.9	4.5
5	0.185	1700	46.9	954	56.1	2.5
6	0.245	1700	58.1	1160	68.2	2.4

First of all we wanted to determine the character of the dependence of the decomposition of $(C_6H_5)_2Hg$ on the amount of oxygen present in the ampoule. From the data obtained (Table 2) it is seen that 1 mol of O_2 corresponds to

different numbers of moles of decomposed diphenylmercury, which increase as the ratio $O_2/(C_6H_5)_2Hg$ decreases.

It was natural to suppose that the decomposition of diphenylmercury would be initiated by peroxide compounds. Therefore, several experiments were carried out with additions of hydroperoxides and peroxides (Table 3). The obtain-

experimental data show that such an effect does indeed exist and is more sharply expressed for peroxide compounds. The radioactivity of the diphenyl isolated in the case of tert-butyl peroxide and hydroperoxide is noteworthy; in different experiments it amounts to a value close to 50% of the activity of the initial benzene

Table 3

Thermal decomposition of diphenylmercury in radioactive benzene in the presence of certain peroxides and hydroperoxides.
$(C_6H_5)_2$ (mol.) : C_6H_5 (mol.) $= 1 : 15$; $t = 260^\circ$

No. of experiment	Additive	Ratio of additive to diphenylmercury	Initial activity of diphenylmercury, imp/min	Duration of heating, h	Decomposition depth, %	Activity of diphenylmercury after the reaction, imp/min	Exchange depth, %	Amount of mercury precipitated relative (mol.) to the additive taken
1	Cumene hydroperoxide	0.044	1890	14	14.4	320	16.9	3.3
2	tert-Butyl hydroperoxide	0.093	1890	14	35.6	520	27.5	3.8
3	Same	0.090	1890	14	34.1	511	27.0	3.8
4	» »	0.090	1890	29	41.96	820	43.4	4.7

No. of experiment	Additive	Ratio of additive to diphenylmercury	Initial activity of diphenylmercury, imp/min	Duration of heating, h	Decomposition depth, %	Activity of diphenylmercury after the reaction, imp/min	Exchange depth, %	Amount of mercury precipitated relative (mol.) to the additive taken
5	Acetone diperoxide	0.034	1890	14	22.7	276	14.6	6.7
6	tert-Butyl peroxide	0.100	1765	2	5.0	31	1.8	0.5
7	Same	0.100	1890	4	42.4	445	23.5	4.2
8	» »	0.100	1890	14	67.8	830	43.9	6.8
9	» »	0.100	1890	14	67.7	814	43.1	6.8
10	» »	0.050	1890	4	27.0	245	13.0	5.4
11	» »	0.050	1890	14	43.8	530	28.0	8.8

(47–51%). This indicates that the diphenyl obtained in the reactions under consideration consists approximately one-half of benzene rings from the solvent.

In the photoreaction of diphenylmercury with benzene (Table 4), in vacuum and in the presence of air, mercury, diphenyl, and a small amount

Table 4

Photodecomposition of diphenylmercury in benzene.
$(C_6H_5)_2$ (mol.) : C_6H_5 (mol.) = 1 : 30

No. of experiment	Initial substances: diphenylmercury, g	Initial substances: diphenylmercury, activity, imp/min	Initial substances: benzene, g	Initial substances: benzene, activity, imp/min	Decomposition depth, %	Substances isolated after the reaction: $(C_6H_5)_2Hg$, activity, imp/min	Substances isolated after the reaction: benzene, activity, imp/min	Substances isolated after the reaction: diphenyl, activity, imp/min	Exchange depth, %	Activity of diphenyl relative to initial activity, %
1	8.00	0	54.7	2020	12.4	2	—	923	0.1	45.7
2	5.59	0	38.2	2020	12.7	2	—	900	0.1	44.5
3	5.64	0	38.6	2020	34.5	7	—	948	0.4	47.0
4	1.9	7190	13.0	0	51.3	—	106	3790	—	52.7

Note. 1. Experiment 1 was carried out in a sealed ampoule in the presence of air. The irradiation was conducted for 175 h. 2. Experiment 2 was carried out in vacuum. Irradiation time 175 h. 3. Experiments 3 and 4 were carried out in ampoules closed with cork stoppers. Irradiation time 175 h. 4. From the activity of the benzene after the reaction (106 imp/min), the amount of radicals from the decomposed diphenylmercury that passed into the solvent in the form of benzene was calculated. This value is 47.3%.

resinous substances, the composition of which we did not determine. It was observed that when the access of air to the reaction mixture is improved, the extent of decomposition of $(C_6H_5)_2Hg$ increases. In contrast to thermal reactions, photoreactions, both in the presence of air and in vacuum, are almost not accompanied by exchange of the phenyl groups of the mercury compound with benzene (about 0.1–0.4%).

It is interesting that the biphenyl formed during the photodecomposition of diphenylmercury consists, to the extent of 44.5–47%, of benzene rings from the solvent (Table 4, experiments 1–3). These data were well confirmed by an experiment on the photodecomposition of labeled $(C_6^{14}H_5)_2Hg$ in ordinary benzene in an atmosphere of air. The biphenyl obtained consisted of 52.7% radicals from the mercury compound. It is noteworthy that the remaining portion (47.3%) of the active radicals of the decomposed diphenylmercury was found as benzene in the solvent.

On the basis of the data obtained in the present work, the following reaction scheme may be proposed:

$$\begin{array}{c} C_6H_5 - C_6^{14}H_5 + Hg + C_6H_6 \\ h\nu \uparrow \\ (C_6H_5)_2Hg + C_6^{14}H_6 \rightleftarrows [(C_6H_5)_2HgC_6^{14}H_6] \\ t^\circ \downarrow \\ [(C_6H_5)(C_6^{14}H_5)HgC_6H_6] \rightleftarrows (C_6^{14}H_5)_2Hg + C_6H_6 \end{array}$$

Diphenylmercury with benzene forms an intermediate complex, within which, on heating, exchange of phenyl radicals takes place.

Under the action of ultraviolet rays the complex decomposes; in this process one phenyl radical of diphenylmercury abstracts hydrogen from benzene, while the other combines with the phenyl group of its molecule. As a result of this act, mercury, benzene, and biphenyl are liberated. The latter consists in equal measure of radicals from the mercury compound and from benzene—the solvent. Oxygen from the air accelerates this process. However, the mechanism of its action is not yet clear to us. The thermal decomposition of diphenylmercury probably proceeds by the same mechanism. But in this case its study with the aid of labeled atoms is made difficult by the presence of exchange reactions between $(C_6H_5)_2Hg$ and benzene.

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