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Abstract

Full Text

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THERMAL DECOMPOSITION AND OXIDATION OF DICYCLOHEXYLMERCURY IN BENZENE

We have previously shown that dicyclohexylmercury (DCHM) (1) is readily oxidized in organic solvents (CCl_4, $CHCl_3$, iso-C_3H_7OH), and it was noted that this compound is sufficiently stable in the absence of atmospheric oxygen. However, in the presence of the latter it readily decomposes at ordinary temperatures. The solvents indicated take part in the reaction during the oxidation of DCHM. It was therefore of interest to trace what products are formed during thermal decomposition in the absence of oxygen without solvents and in an inert solvent, such as benzene. The decomposition of DCHM is not described in the literature.

Table 1

Decomposition of DCHM in benzene at 200°, 50 h.

Reaction products	Amount, moles	Amount, mol. percent relative to mercury isolated
Hg	0.021	100
C_6H_{12} (cyclo)	0.0276	131.4
C_6H_{10} (cyclo)	0.0031	14.8
C_6H_{11}—C_6H_{11}	0.0017	8
DCHM	0.001	4.5
C_6H_{11}—C_6H_5	0.0004	2
Distillation residue*	0.0065	31

Thermal decomposition of DCHM was carried out at 180° in the absence of atmospheric oxygen for a sufficiently long time (40–50 h) in order to attain complete decomposition. DCHM decomposed practically completely with separation of mercury and formation of cyclohexane, cyclohexene, and dicyclohexyl; the latter distilled over during steam distillation. In the flask there remained a product in the form of a solid brown substance, readily soluble in $CHCl_3$ and insoluble in methanol. After two precipitations with methanol from a chloroform solution it was a white substance, close in composition to $(C_6H_9)_x$. The results obtained are given below.

Reaction products	Amount, mol. %
Hg	100
c-C_6H_{12}	120
c-C_6H_{10}	30
C_6H_{11}—C_6H_{11}	10
Distillation residue*	20–25

During decomposition of DCHM (0.022 mole) in benzene (0.11 mole) at 200° for 50 h, the principal products were cyclohexane, cyclohexene, dicyclohexyl, and mercury, i.e., the same as in the process indicated above. Phenylcyclohexane was also found in small amount. The experimental data are given in Table 1.

After removal from the reaction product, by vacuum distillation, of benzene, cyclohexane, and cyclohexene, there remained a brown viscous oil, in which, by IR spectra, dicyclohexyl and phenylcyclohexane (about 2%) were found. This oil contained about 4.5% undecomposed DCHM. Poafter distillation with steam, a solid substance also remained in the flask as the main product, close in composition to $(C_6H_9)_x$. It could be expected that the decomposition of DCHM in benzene would proceed according to the scheme proposed for diphenylmercury (^{2}):

$$(C_6H_5)_2Hg + {}^*C_6H_6 \rightarrow [(C_6H_5)_2Hg \cdot {}^*C_6H_6] \rightarrow Hg + C_6H_6 + C_6H_5 \cdot {}^*C_6H_5$$

through an intermediate complex, with formation of mercury, cyclohexane, and phenylcyclohexane. However, the latter product was found in an insignificant amount.

Judging from the reaction products, it may be assumed that the decomposition of DCHM proceeds either in a cage according to the scheme

$$(C_6H_{11})_2Hg \rightarrow Hg + [2C_6H_{11}\bullet]$$

$$[2C_6H_{11}\bullet] \begin{cases} \rightarrow C_6H_{12} + C_6H_{10}, \\ \rightarrow C_6H_{11}\text{—}C_6H_{11}, \end{cases}$$

with disproportionation and, to a lesser extent, dimerization of C_6H_{11}-radicals, or else by decomposition initiated by cyclohexyl radicals:

* A solid substance of composition $(C_6H_9)_x$, the content of which was calculated relative to the C_6H_{11} group.

$$C_6H_{11}\bullet + (C_6H_{11})_2Hg \rightarrow C_6H_{12} + C_6H_{11}HgC_6H_{10}$$

$$\downarrow$$

$$C_6H_{11}\bullet + Hg + C_6H_{10}$$

The choice of one or the other scheme requires additional investigations.

From Table 1 it is seen that considerably less cyclohexene is formed than cyclohexane. This can be explained by the side process of interaction of c-C_6H_{11}-radicals with the cyclohexene being formed, with an additional yield of cyclohexane and a cyclohexenyl radical. In this case a solid substance is formed, close in composition to $(C_6H_9)_x$:

$$C_6H_{11}\bullet + C_6H_{10} \rightarrow C_6H_{12} + C_6H_9\bullet$$

$$xC_6H_9\bullet \rightarrow (C_6H_9)_x.$$

Similar dehydropolymerization of cyclohexene was observed during the thermal decomposition of diphenylmercury (^{4}) and di-tert-butyl peroxide (^{4}) in this olefin. During the oxidation of DCHM in benzene by free oxygen at room temperature and at 60°, the solvent also takes an insignificant part in this process.

Table 2

Oxidation of DCHM (0.015 mole) in benzene (0.12 mole) at 60°, 70 h.
(About 0.02 mole of oxygen was absorbed)

Reaction products	Amount, in moles	Amount, in mole percent with respect to mercury evolved
Hg	0.014	100
$C_6H_{11}OH$ (cyclo)	0.0063	57.3
$C_6H_{10}O$ (cyclo)	0.005	45.5
C_6H_{12} (cyclo)	0.0055	50
C_6H_{10} (cyclo)	0.0022	20
$C_6H_5—C_6H_5$	0.0006	5.4

Thus, upon oxidation of DCHM at 60°, the main reaction products are cyclohexanol, cyclohexanone, cyclohexane, cyclohexene, and mercury. A small content of diphenyl was also found (5.4%). The results are given in Table 2. Along with oxidation products, a considerable yield of disproportionation products—cyclohexane and cyclohexene—is observed, and with decreasing temperature the yield of the latter decreases. Thus, upon oxidation of DCHM (0.003 mole) in benzene (0.2 mole) at 20–25°, mainly only cyclohexanol and cyclohexanone were formed (0.0018 mole, which corresponded to 90 mole % of each with respect to the decomposed DCHM).

At ordinary temperature the oxidation process of DCHM can be represented by the equation:

$$(C_6H_{11})_2Hg + O_2 \rightarrow [(C_6H_{11})_2Hg \cdot O_2] \rightarrow C_6H_{11}OH + C_6H_{10}O + Hg.$$

However, at elevated temperatures, in addition to these products formed according to this scheme, a considerable yield of the same products as in thermal decomposition is observed. In the present case this cannot be explained by thermal decomposition of DCHM, since the reaction temperature (60°) is quite insufficient for its decomposition. As we showed earlier ([1]), it begins to decompose above 130°. This can be explained only by decomposition of DCHM initiated by the intermediate peroxide compound, which is also consistent with the previously noted fact of its instability on storage in air.

The formation of diphenyl during the oxidation of DCHM in benzene can apparently be explained by dimerization of phenyl radicals, the source of generation of which is more likely to be $RO\bullet$ than R-radicals. In support of this fact, first, during the thermal decomposition of DCHM in the absence of oxygen, appreciable amounts of diphenyl were not detected; second, the oxidation products—cyclohexanol and cyclohexanone—are formed in nonequimolecular amounts, the former by approximately 12% more, which corresponds to the amount of phenyl groups in the diphenyl formed (Table 2). Hence it must be assumed that the intermediate peroxide compound of DCHM that is formed decomposes not only intramolecularly with formation of equimolecular amounts of oxidation products and mercury, which seemed to us more probable, but also with formation of RO-radicals; the RO-radical, interacting with benzene, gives cyclohexanol and a secondary phenyl radical.

Thus, on the basis of the experimental data it may be concluded that both the thermal decomposition and the oxidation of DCHM in benzene proceed by a free-radical mechanism.

The products were analyzed by the procedure described above ([1,3]).

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REFERENCES CITED

1. G. A. Razuvaev, G. G. Petukhov et al., DAN, **135**, 87 (1960).

2. G. A. Razuvaev, G. G. Petukhov, Yu. A. Kaplin, DAN, **135**, 342 (1960).

3. G. A. Razuvaev, G. G. Petukhov et al., DAN, **141**, 371 (1961).

4. E. N. Farmer, C. G. Moore, *J. Chem. Soc.*, **1951**, 131.

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

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