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Abstract

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OXIDATION OF DIISOPROPYLMERCURY

In a previous communication (^{1}), the oxidation of dicyclohexylmercury (DCHM) in various solvents was investigated. Naturally, the question arose whether other organomercury compounds with secondary carbon radicals would also react with oxygen. For this purpose we tested the simplest representative of this class—diisopropylmercury (DIPM). According to the literature (^{2}), DIPM is a colorless liquid boiling at 119—121°/125 mm. This compound, when stored in air, liberates mercury. We believe that the cause of this is the action of oxygen, as was established in the case of DCHM. Indeed, DIPM is readily oxidized by atmospheric oxygen even under ordinary conditions.

In the present work we studied certain processes of the oxidation of DIPM in isopropyl alcohol, carbon tetrachloride, and chloroform. In a solution of isopropyl alcohol, oxidation liberates mercury and produces a considerable amount of acetone. In addition, isopropyl alcohol should also have been expected among the oxidation products. In this case the formation of the latter could be confirmed only by using a labeled compound.

Indeed, using C^{14}-DIPM, we detected labeled isopropyl alcohol in the reaction products. Thus, the process may be represented in general form by the equation

$$(\text{iso-}C_3H_7)_2Hg + O_2 \rightarrow [(-C_3H_7)_2Hg \cdot O_2] \rightarrow Hg + (CH_3)_2CO + (CH_3)_2CHOH. \quad (1)$$

Considerably more acetone and alcohol are formed than would correspond to the above equation. This discrepancy may be explained by the simultaneous oxidation of the solvent—isopropyl alcohol—to acetone. A similar phenomenon was noted earlier in the oxidation of DCHM. The experiments we carried out do in fact confirm oxidation of the solvent. Thus, in the oxidation of C^{14}-DIPM in isopropyl alcohol (molar ratio 1 : 28) for 11 hr at 65—66°, the activity of the acetone (4450 imp/min) amounted to only about 20% of the activity (22400 imp/min) of the initial organomercury compound. The lowered activity of the acetone is explained by its dilution through oxidation of the solvent—isopropyl alcohol. The isopropyl alcohol after the reaction also contained activity of 670 imp/min.

The amount of alcohol and acetone formed from C^{14}-DIPM was calculated from their relative activity. Their contents were, respectively, about 158 and 43 mol.% based on the mercury liberated.

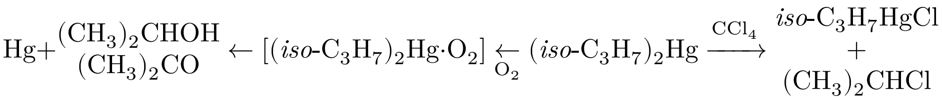
The formation of acetone from the solvent was also confirmed by oxidizing DIPM in C^{14}-isopropyl alcohol (molar ratio 1 : 23). The activity of the acetone (3040 imp/min) amounted to about 55% of the activity

(5540 imp/min) of the initial alcohol when the reaction was carried out at 66–67° for 15 h.

Depending on the experimental conditions, the amount of acetone formed through oxidation of the solvent varied from 150 to 400 mol.%.

The reaction proceeds in a more complicated manner in chlorine-containing solvents, CCl_4 and $CHCl_3$. The data obtained show that the solvent reacts with DIPM to form isopropylmercury chloride, $iso\text{-}C_3H_7HgCl$ (about 70%), and, in the case of CCl_4, isopropyl chloride.

In these solvents the reaction may be represented by the following general scheme:



$$\mathrm{Hg}+\begin{matrix}(\mathrm{CH_3})_2\mathrm{CHOH}\\(\mathrm{CH_3})_2\mathrm{CO}\end{matrix} \leftarrow [(iso\text{-}\mathrm{C_3H_7})_2\mathrm{Hg}\cdot\mathrm{O_2}] \underset{\mathrm{O_2}}{\leftarrow} (iso\text{-}\mathrm{C_3H_7})_2\mathrm{Hg} \xrightarrow{\mathrm{CCl_4}} \begin{matrix} iso\text{-}\mathrm{C_3H_7HgCl}\\ + \\ (\mathrm{CH_3})_2\mathrm{CHCl}\end{matrix} \qquad (2)$$

On the one hand, the oxidation of DIPM described above proceeds with formation of Hg, alcohol, and acetone; on the other hand, there is an interaction of CCl_4 ($CHCl_3$) with the organomercury compound, initiated by the intermediate peroxide compound. According to literature data (^{3}), it is known that acyl peroxides initiate the interaction of an organomercury compound with CCl_4. The predominance of one or the other pathway depends on the process conditions. With an increase in temperature, the amount of chlorine-containing reaction products formed increases sharply (Table 1).

Table 1

Oxidation of DIPM in CCl_4 and $CHCl_3$

Reaction products	CCl_4 *	CCl_4 **	$CHCl_3$ *
Hg	14.3	0	28.6
$iso\text{-}C_3H_7HgCl$	71.4	85.7	71.2
$(CH_3)_2CO$	54.3	33.0	60.0
$(CH_3)_2CHOH$	11.4	0	28.6
$(CH_3)_2CHCl$	11.4	44.3	–

Mol.% relative to DIPM.

* Reaction at 17–20° for 20 h. Taken: 0.0035 mol DIPM per 0.09 mol solvent.
** Reaction at 44° for 18 h. Taken: 0.007 mol DIPM per 0.09 mol solvent.

In the oxidation products, the ratio of alcohol to acetone was about 1 : 2 in $CHCl_3$ and 1 : 5 in CCl_4. This ratio is probably explained by oxidation of the isopropyl alcohol formed to acetone in these systems. In addition to the compounds indicated, in CCl_4 at elevated temperature other compounds not identified by us are formed, having absorption bands of esters and acid chlorides.

In the reaction products, the content of isopropyl alcohol and isopropyl chloride was determined on an IKS-14 infrared spectrophotometer from a calibration curve constructed using standards in the corresponding solvents in the coordinates: optical density (D)—concentration ($C, \%$). The acetone content was determined by titration of hydrochloric hydroxylamine. Oxidation was carried out in ampoules connected by means of a polyethylene tube to an oxygen-filled burette; the reaction mixture was stirred with a mechanical stirrer.

Oxidation of DIPM in isopropyl alcohol was carried out in sealed ampoules in an oxygen atmosphere with shaking.

In the reaction product, the amount of acetone and its activity were determined on an internal-flow counter by combustion of the corresponding 2,4-dinitrophenylhydrazone, m.p. 125° (ethanol).

The filtrate from the hydrazone was diluted with unlabeled acetone, followed by precipitation of its excess with hydrochloric acid solution of 2,4-dinitrophenylhydrazine. After this the filtrate was distilled. A small first fraction was collected, dried, and redistilled. In this fraction the activity of the isopropyl alcohol after the reaction was determined.

The results of oxidation of DIPM in CCl_4 and $CHCl_3$ are given in Table 1.

The reaction mixture was distilled under vacuum. Mercury and isopropylmercury chloride remained in the residue; the latter is, in the form of needles, crystals (from acetone) with m.p. 93–94°.

Found, %:	Hg 71.38; Cl 12.73
C_3H_7HgCl. Calculated, %:	Hg 71.87; Cl 12.72

A quantitative analysis of the components was carried out in the distilled fraction. For the quantitative analysis of isopropyl alcohol, the absorption band with frequency 950 cm^{-1} in CCl_4 and $CHCl_3$ was used; for isopropyl chloride, 615 cm^{-1}.

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