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OXIDATION OF ALKYL ORGANOMERCURY COMPOUNDS

Earlier we showed that secondary alkyl organomercury compounds—dicyclohexyl-([1]) and diisopropylmercury ([2]) (DIPM)—are oxidized at ordinary temperature by oxygen both without a solvent and in solutions, with liberation of mercury and formation of the corresponding alcohols, ketones, and hydrocarbons. In that work the main attention was directed to the oxidation and detachment from mercury of radicals. In the present communication we have dealt with a more detailed investigation of the process, in which special attention was given to elucidating the formation of any oxidized organomercury compounds. The oxidation of symmetrical mercury compounds with primary (benzyl-), secondary (isopropyl-), and tertiary (tert-amyl-) alkyl radicals was studied. The reaction products were analyzed by chemical and physicochemical methods, with the use of mass spectrometry, gas chromatography, and infrared spectroscopy.

The oxidation of DIPM in benzene, cyclohexane, cyclohexene, $CHCl_3$, and CCl_4 was studied in detail. The principal reaction products in benzene are isopropylmercury isopropylate, isopropylmercury hydroxide, acetone, isopropyl alcohol, and mercury. In the gaseous space above the reaction mixture, propylene and traces of propane were detected. Benzene took almost no part in the reaction. The presence of its derivatives (phenylisopropylmercury, diphenylmercury, diphenyl, phenol, and cumene) was detected in small quantity by mass spectrometry. In a specially conducted experiment with C^{14}-benzene it was established that their total yield was not more than 5 mol.% relative to the initial DIPM. Isopropylmercury isopropylate and isopropylmercury hydroxide were identified by low-voltage mass spectrometry, and their amount was determined in total by titration of hydroxides with 0.1 N HCl with methyl orange after preliminary hydrolysis of the reaction product with water. After the hydrolysis carried out, isopropyl alcohol was detected in the extract, which confirms the formation of iso-

Table 1

Oxidation of 0.007, 0.0031, and 0.0031 moles of DIPM, respectively, in 0.11, 0.046, and 0.046 moles of C_6H_6, C_6H_{12}, and C_6H_{10} at 50° C

Reaction products	C_6H_6, 30 h: in moles	C_6H_6, 30 h: in mol.%*	C_6H_{12}, 25 h: in moles	C_6H_{12}, 25 h: in mol.%*	C_6H_{10}, 25 h: in moles	C_6H_{10}, 25 h: in mol.%*
Hg	0.0017	33.3	0.0008	30	0.001	40
iso-C_3H_7OHg-iso-C_3H_7 }	0.0034	66.7	0.0019	70	–	–
iso-C_3H_7HgOH }	0.0034	66.7	0.0019	70	0.0015	60
$(CH_3)_2CO$	0.003	58.8	0.0012	44.4	0.0009	36
iso-C_3H_7OH	0.0013	25.5	0.0006	22.2	0.0024	96
C_3H_8	traces	–	traces	–	0.0002	8
C_3H_6	0.0001	2	0.0001	3.7	traces	–
Oxidation products of the solvent	traces	–	traces	–	0.005**	200

* Relative to reacted DIPM.
** Calculated as the C_6H_9 group.

propylmercury isopropoxide during oxidation of DIPR (Table 1). It was established that their content at first increased and then remained constant during prolonged oxidation at 50°.

A similar picture in the ratio of the same reaction products (Table 1) is observed when this compound is oxidized in cyclohexane.

In both the first and the second solvent, approximately twice as much ketone as alcohol is formed. This can be explained by the comparatively easy oxidation of the alcohol formed to acetone. Formation of the latter was in fact observed at the expense of the solvent during oxidation of dicyclohexylmercury (^{1}) and DIPR (^{2}) in isopropanol. Oxidation of DIPR in cyclohexene proceeds differently: the yield of isopropyl alcohol is higher than that of acetone; propane is formed instead of propylene; the balance for isopropyl radicals indicates the absence of mercury alkoxy compounds and the presence of hydroxide; in the course of the reaction this solvent undergoes considerable oxidation (Table 1). Mass-spectrometric analysis showed the absence of isopropylmercury isopropoxide.

We believe that the formation of hydroxide in all solvents occurs as a result of the easy hydrolysis of isopropylmercury isopropoxide by the moisture present or by water formed in the reaction. The latter is, in all probability, one of the products of cyclohexene oxidation. Upon hydrolysis of the alkoxy compound, isopropyl alcohol should be obtained along with mercury hydroxide. Its considerable yield in comparison with acetone is indeed observed in the oxidation of DIPR in cyclohexene.

The participation of $CHCl_3$ in the reaction was indicated earlier ([2]). We repeated the experiment, carrying it out at 50° (Table 2). It was noted that the mercury liberated at the beginning of the oxidation disappeared, evidently being converted into calomel, whose presence was established. Among products not indicated earlier, propane, propylene, CO_2, and CO should be noted, the last two being formed at the expense of the solvent.

Table 2

Oxidation of 0.0032 and 0.005 moles of DIPR, respectively, in 0.062 and 0.083 moles of $CHCl_3$ and CCl_4

Reaction products	$CHCl_3$, 50° C, 40 h: in moles	$CHCl_3$, 50° C, 40 h: in mole % relative to DIPR	CCl_4, 60° C, 20 h: in moles	CCl_4, 60° C, 20 h: in mole % relative to DIPR
Hg	traces	–	0.0003	6
HgCl	0.0004	12.5	traces	–
iso-C_3H_7HgCl	0.0026	81.2	0.0046	92
$(CH_3)_2CO$	0.0016	50	0.0015	30
iso-C_3H_7OH	0.0011	34.4	0.0002	4
iso-C_3H_7Cl	–	–	0.0024	48
C_3H_8	0.0007	21.9	traces	–
C_3H_6	0.0001	3.1	0.0001	2
CO	0.0008	25	0.0005	10
CO_2	0.0004	12.5	0.001	20
$CHCl_3$	–	–	0.0015	30

Oxidation of DIPR in CCl_4 proceeds somewhat differently. The yield of alcohol and acetone is lower than in $CHCl_3$, while the greater part of the isopropyl radicals reacts with the solvent to form 2-chloropropane. In addition to CO and CO_2, formation of $CHCl_3$ and hexachloroethane at the expense of CCl_4 is observed (Table 2).

Tertiary-alkyl mercury compounds are also readily oxidized. Ditert-amylmercury behaves analogously to DIPR in the corresponding solvents. Table 3 gives the results of its oxidation in $CHCl_3$, CCl_4, benzene, and cyclohexane. In C_6H_6 and -C_6H_{12} we were unable to titrate hydroxide. The product decomposed with water with liberation of mercury and did not have an alkaline reaction. Evidently, the alkoxy compound or hydroxide of tert-amylmercury is unstable in water and decomposes with liberation of mercury.

Consequently, not only secondary- but also tertiary-alkyl mercury compounds are affected by oxygen. Using dibenzylmercury as an example, the possibility of oxidation of primary mercurialkyls was shown qualitatively. In the oxidation of this compound in $CHCl_3$, CCl_4, and C_6H_6, one of the reaction products is benzaldehyde. Thus, in the reaction of 0.0064 moles

Table 3

Oxidation of 0.0055, 0.0055, 0.0019, and 0.0029 moles of ditertiaryamylmercury, respectively, in 0.062, 0.075, 0.056, and 0.074 moles of CCl_4, $CHCl_3$, C_6H_6, and C_6H_{12} at 40° C

Reaction products	CCl_4, 30 h, in moles	CCl_4, 30 h, mole %	$CHCl_3$, 30 h, in moles	$CHCl_3$, 30 h, mole %	C_6H_6, 25 h (50°), in moles	C_6H_6, 25 h (50°), mole %	C_6H_{12}, 20 h, in moles	C_6H_{12}, 20 h, mole %
Hg	0.0006	10.9	0.0008	14.5	0.0011	57.8	0.0014	48.3
tert.-$C_5H_{11}HgCl$	0.0044	80	0.004	72.7	–	–	–	–
tert.-$C_5H_{11}OH$	0.0011	20	0.0018	32.7	0.0012	63.2	0.0017	58.6
$(CH_3)_2CO$	0.0016	29.1	0.0018	32.7	0.0009	47.4	0.0013	44.8
2-methylbutene-2	0.0015	27.3	0.0014	25.5	0.0007	36.8	0.0006	20.7
2-methylbutane	0.0002	3.6	0.0005	9.1	0.0002	10.5	traces	–
tert.-$C_5H_{11}Cl$	0.0018	32.7	–	–	–	–	–	–
CO_2	0.001	18.2	0.0007	12.7	–	–	–	–
CO	0.001	18.2	0.0005	9.1	–	–	–	–

On oxidation of dibenzylmercury in 0.23 mole of C_6H_6 at 50° for 120 h, 0.0016 mole (25%) of mercury was isolated and 0.002 mole (31%) of benzaldehyde was formed.

Apparently, susceptibility to oxidation is a general property of alkyl organomercury compounds, which, to one degree or another, under definite conditions are affected by oxygen.

The mechanism of oxidation of organomercury compounds is rather complex. For a complete understanding of it, kinetic studies are required; however, on the basis of the results obtained the following conclusions may be drawn. The oxidation process proceeds with formation of an intermediate organomercury peroxide compound:

$$\mathrm{R_2Hg + O_2 \to [R_2Hg \cdot O_2] \to [ROO{-}HgR]} \begin{cases} \xrightarrow[\mathrm{R_2Hg}]{} \mathrm{2ROHgR} & \text{(a)} \\ \longrightarrow \mathrm{RO_2^{\cdot} + RHg^{\cdot}} & \text{(b)} \end{cases} \qquad (1)$$

The attack of oxygen directed at the metal is accompanied by subsequent nucleophilic migration of the alkyl group from the metal to oxygen with formation of the indicated peroxide. The latter reacts with the unoxidized organomercury compound (a), giving an alkoxy compound, or partially decomposes (b), owing to its instability, into peroxyalkyl and alkylmercury radicals. A similar scheme is given by many authors to explain the oxidation of organometallic compounds of various metals (^{3}).

The peroxyalkyl radical apparently reacts as an oxidizing agent with the starting compound, with formation of an alcohol, ketone, and alkylmercury radical.

$$\mathrm{RO_2^{\cdot} + R_2Hg \to ROH + R_{-H}{=}O + RHg^{\cdot}} \qquad (2)$$

For a tert-alkyl peroxide radical, its decomposition with destruction of the carbon skeleton at the tertiary carbon atom into a ketone (in our case, the formation of acetone is observed) and an alkoxy radical is characteristic:

$$\mathrm{C_2H_5(CH_3)_2CO_2^{\cdot} \to (CH_3)_2CO + C_2H_5O^{\cdot}} \qquad (3)$$

It is known from the literature (^{4}) that such a process takes place and proceeds readily on a surface; in the present case it is promoted by the mercury liberated in the course of the reaction. From the data of Table 3 it is seen that acetone is formed in considerable amounts. The fate of the ethoxyl radical was not established by us.

Evidence for the participation of the alkylmercury radical in the reaction is the significant yield of alkylmercury chloride in $CHCl_3$ and CCl_4, whose formation –

can be represented by the equation:

$$\begin{array}{ccc} \mathrm{RHg^{\bullet}} & \xrightarrow{\mathrm{CCl_4(CHCl_3)}} & \mathrm{RHgCl.} \\ & \downarrow & \\ & \mathrm{Hg + R^{\bullet}} & \end{array} \qquad (4)$$

This radical also partially decomposes into mercury and an alkyl radical. The participation of the latter is manifested in its interaction with $CHCl_3$, with formation of a hydrocarbon, or with CCl_4, with formation of an alkyl chloride:

$$R^\bullet \begin{cases} \xrightarrow{CHCl_3} RH + Cl_3C^\bullet \\ \xrightarrow{CCl_4} RCl + Cl_3C^\bullet \end{cases} \tag{5}$$

As already indicated, in CCl_4 the yield of oxidation products of diisopropylmercury is lower than in $CHCl_3$, while isopropyl chloride is formed in a fairly significant amount. In the present case, in addition to reactions (4) and (5), one should assume an interaction, initiated by an intermediate peroxide compound, of dialkylmercury with the solvent, with formation of alkylmercury chloride and alkyl chloride. It is known (^{5}) that acyl peroxides initiate the interaction of organomercury compounds with CCl_4.

In $CHCl_3$ and CCl_4, secondary dichloro- and trichloromethyl radicals, respectively, should be formed. In the case of the former, we did not detect the product of its dimerization. It may be assumed that it is oxidized to CO_2 and CO, which are present in the reaction products. In CCl_4, formation of CO_2 and CO is likewise observed, as well as, in the case of diisopropylmercury, chloroform and hexachloroethane. $CHCl_3$, evidently, is formed by interaction of the trichloromethyl radical chiefly with the isopropyl alcohol formed (^{6}), and to a lesser extent with diisopropylmercury, as indicated by the insignificant yield of propylene.

Thus, it has been established experimentally that alkyl organomercury compounds are capable of being oxidized, the ease of oxidation increasing in the order of increasing nucleophilicity in the following sequence:

$$CH_3CH_2-CH_2-, \quad C_6H_5-CH_2-, \quad (CH_3)_2-CH-, \quad C_2H_5(CH_3)_2-C-,$$

i.e., it is evidently due to the different ability of alkyl radicals to undergo nucleophilic rearrangement in the intermediate complex $[R_2Hg \cdot O_2]$.

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

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