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Abstract

Full Text

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STUDY OF THE INTERACTION OF DIPHENYLMERCURY WITH ALCOHOLS BY ISOTOPIC AND MASS-SPECTROMETRIC METHODS

Previously ([1]), the photoreaction of diphenylmercury with alcohols was studied; it proceeds with formation of benzene, mercury, and an aldehyde or ketone for a primary or secondary alcohol, respectively. It was shown that, upon dissociation of the mercury compound, the species formed

$$\begin{array}{c} (C_6H_5)_2Hg \rightarrow C_6H_5\cdot + C_6H_5Hg\cdot \\ \downarrow \\ C_6H_5\cdot + Hg \end{array} \quad (1)$$

phenyl radicals abstract hydrogen from the carbon atom of the alcohol bound to the hydroxyl group, but not the hydrogen of the hydroxyl itself. In particular, for isopropyl alcohol the following process takes place:

$$C_6H_5\cdot + (CH_3)_2CHOH \rightarrow C_6H_6 + (CH_3)_2\dot{C} - OH. \quad (2)$$

It was assumed that the secondary alcohol radical thus formed then disproportionates:

$$2(CH_3)_2\dot{C} - OH \rightarrow (CH_3)_2CHOH + CH_3COCH_3. \quad (3)$$

Free radicals may also initiate the decomposition of organomercury compounds ([2]). In the present case, the following process may be expected:

$$(CH_3)_2\dot{C} - OH + C_6H_5HgC_6H_5 \rightarrow (CH_3)_2CO + C_6H_6 + C_6H_5Hg. \quad (4)$$

An initiated decomposition of this kind was observed in the reaction of diisopropyl percarbonate with isopropyl alcohol ([3]).

The use of labeled compounds in combination with the mass-spectrometric method of analysis is often the only means of studying the mechanisms of various chemical processes. We used isotopic and mass-spectrometric methods for a more detailed study of the mechanism of the interaction of diphenylmercury with alcohols. We studied the photo- and thermoreactions of diphenylmercury with tert-butyl and isopropyl alcohols labeled with deuterium both in the α-position and in the hydroxyl.

It should be noted that the rate of photolysis of diphenylmercury in tert-butyl alcohol is lower than in isopropyl alcohol. This is evidently due to the absence of hydrogen at the α-carbon atom.

In the photoreaction of diphenylmercury with isopropyl alcohol, mercury, benzene, acetone, diphenyl, and also a mercury-containing brown substance insoluble in alcohols, ether, or benzene are formed (Table 1).

In the case of the reaction with tert-butyl alcohol, isobutylene (a dehydration product of the alcohol), methane, and ethane are also formed (Table 1). The presence of acetone is due to decomposition of the tertiary butoxy radical ([4]):

$$(CH_3)_3CO\cdot \rightarrow (CH_3)_2CO + CH_3\cdot \tag{5}$$

The methyl radicals that appear dimerize to ethane or abstract hydrogen from the solvent, thereby becoming methane.

In the reaction products of diphenylmercury with the indicated alcohols, the presence of diphenyl was observed. Since its yield is small, its amount was calculated from the difference between the phenyl radicals of the decomposed diphenylmercury and the benzene formed.

From the isotopic composition of benzene it was established that phenyl radicals abstract hydrogen from isopropyl alcohol predominantly from the α-position. As is seen from the data in Table 1, formation of deuteriobenzene is observed to an extent of no more than 10% when the reaction is carried out in alcohols labeled in the hydroxyl group, as against 66% for alcohol labeled in the α-position (calculated for 100% deuterium in the alcohol, without allowing for kinetic isotope effects). These results indicate that reaction (2) takes place.

Table 1

Photolysis of 0.001 mole of $(C_6H_5)_2Hg$ in 0.03, 0.04, and 0.04 moles of tert-C_4H_9OD (47% D), $(CH_3)_2CHOD$ (70% D), and $(CH_3)_2CDOH$ (90% D), respectively

Reaction products	tert-C_4H_9OD, 25 h, mol.%	$(CH_3)_2CHOD$, 13 h, mol.%	$(CH_3)_2CDOH$, 13 h, mol.%
Hg	74	90	80
C_6H_6*	120	170	150
$(CH_3)_2CO$	14	70	60
$(C_6H_5)_2$**	14	5	5
$(CH_3)_2C{=}CH_2$	10	–	–

Reaction products	tert-C_4H_9OD, 25 h, mol.%	$(CH_3)_2CHOD$, 13 h, mol.%	$(CH_3)_2CDOH$, 13 h, mol.%
CH_4	4	–	–
C_2H_6	7	–	–

* Isotopic composition of benzene, in %:

Alcohol	C_6H_6	C_6H_5D
tert-C_4H_9OD	95.1 (89.6)	4.8 (10.2)
$(CH_3)_2CHOD$	95.8 (94)	4.1 (5.9)
$(CH_3)_2CDOH$	40.5 (33.8)	59.4 (66.1)

** Isotopic composition of diphenyl, in %:

$C_{12}H_{10}$	$C_{12}H_9D$	$C_{12}H_8D_2$
93.9	5.4	0.7
91.9	6.7	1.4
73.3	26.1	0.6

Note. The values in parentheses are those calculated for 100% deuterium in the alcohols without allowance for the kinetic isotope effect.

In the interaction of diphenylmercury with alcohols labeled in the hydroxyl group, the formation of monodeuteriobenzene is observed in small amount. It could have been formed as the result of the side reaction (6), discussed below; of the process represented by equation (4); or as the result of abstraction of hydroxyl deuterium by phenyl radicals (5). The presence in the methane liberated in the photoreaction of diphenylmercury with tert-C_4H_9OD of about 1% of the CH_3D form indicates the possibility of such abstraction under the given conditions.

The isotopic composition of the benzene from the reaction of the organomercury compound with $(CH_3)_2CDOH$ (allowing for benzene in whose formation the hydroxyl hydrogen of the alcohol participates) does not correspond to the isotopic composition of the starting alcohol (Table 1). This discrepancy is evidently due to the isotope effect (K_H/K_D) for abstraction of hydrogen (deuterium) from the α-position of the alcohol by phenyl radicals. Thus, it is known [6] that $K_H/K_D = 8.7 \pm 2.3$ (30°) for abstraction of hydrogen (deuterium) from the methyl group of methanol by CD_3 radicals. In our case, if the lowered content of the C_6H_5D species is taken as the result of a kinetic isotope effect, we obtain

$$K_H/K_D = \frac{\%D \text{ in the solvent}}{\%H \text{ in the solvent}} \cdot \frac{\%H \text{ in benzene}}{\%D \text{ in benzene}} = 4.4.$$

Disproportionation of the alcohol radical $(CH_3)_2\dot{C}{-}OH$ formed in reaction (1) can be demonstrated by using an alcohol labeled with heavy hydrogen in the hydroxyl group. In the event of disproportionation of this radical according to equation (3), an alcohol labeled in the α-position, $(CH_3)_2CDOD$, should appear. Mass-spectrometric analysis of the isotopic composition of the alcohol, in which the hydroxyl deuterium had first been completely exchanged for the light isotope, showed that the ratio of the intensities of the principal lines with $m/e = 46$ and $m/e = 45$, correspond-

forms $(CH_3)_2CDOH$ and $(CH_3)_2CHOH$ is higher in the alcohol isolated from the reaction than in the initial alcohol. This fact indicates migration of the label from the hydroxyl group to the α-position, which evidently occurs by disproportionation of the alcohol radical $(CH_3)_2\dot{C}{-}OD$, formed in the photolysis reaction of diphenylmercury. It was calculated that the content of the form $(CH_3)_2CDOH$ is $1.5 \pm 0.1\%$ of the alcohol taken. Recalculated to 100% deuterium alcohol $(CH_3)_2CHOD$, this corresponds to an $85 \pm 5\%$ yield of the indicated alcohol. On the other hand, when the reaction is carried out in alcohol labeled in the α-position, it was established that the latter is diluted (by $1.1 \pm 0.1\%$, which corresponds to a yield of $44 \pm 4\%$) with the form $(CH_3)_2CHOH$. This, in all probability, is due to disproportionation of the $(CH_3)_2\dot{C}{-}OH$ radicals. The amount of protium alcohol formed according to equation (3) at the expense of the indicated alcohol radicals should correspond to half the yield of deuterobenzene ($89 : 2 = 44.5\%$), which is indeed observed.

Thus, on the basis of the data obtained, it may be concluded that the secondary alcohol radicals $(CH_3)_2\dot{C}{-}OH$ (D) formed in the photoreaction predominantly disproportionate according to equation (3).

Table 2

Decomposition of 0.001, 0.0015, and 0.001 mole of $(C_6H_5)_2Hg$ in 0.03, 0.03, and 0.025 mole of tert-C_4H_9OD (47% D), $(CH_3)_2CHOD$ (75% D), and $(CH_3)_2CDOH$ (90% D), respectively

Reaction products	tert-C_4H_9OD220-240°,70 h	$(CH_3)_2CHOD$190-200°,30 h	$(CH_3)_2CDOH$190-200°,20 h
	mol. %	mol. %	mol. %
Hg	80	93.4	90
C_6H_6 *	140	173	170
$(CH_3)_2CO$	10	80	70
$(C_6H_5)_2$ **	10	7	5
$(CH_3)_2{=}CH_2$	20	–	–
CH_4	5	–	–
C_2H_6	2	–	–

* Isotopic composition of benzene, in %:

Alcohol	C_6H_6	C_6H_5D	$C_6H_4D_2$
tert-C_4H_9OD	65.5 (26.5)	32.0 (68.2)	2.4 (5.1)
$(CH_3)_2CHOD$	36.8 (15.8)	58.9 (78.5)	4.1 (5.5)
$(CH_3)_2CDOH$	99.5 (99.4)	0.5 (0.6)	–

** Isotopic composition of diphenyl, in %:

$C_{12}H_{10}$	$C_{12}H_9D$	$C_{12}H_8D_2$	$C_{12}H_7D_3$
59.3	31.3	7.6	1.6
37.0	46.0	13.0	3.5
98.3	1.3	0.4	–

Note. The values in parentheses are those calculated for 100% deuterium alcohols without allowance for the kinetic isotope effect.

The interaction of diphenylmercury with alcohols proceeds quite differently in thermal reactions. As is seen from the data in Table 2, the hydroxyl hydrogen takes predominant part in the formation of benzene. Deuterobenzene is practically not formed in the decomposition of diphenylmercury in alcohol labeled in the α-position under the given conditions. These results indicate a different reaction mechanism. Namely, the interaction of diphenylmercury proceeds through the formation of an intermediate reaction complex, decomposing into benzene and, evidently, an alkoxy compound of mercury:

$$\left[\begin{array}{c} C_6H_5HgC_6H_5 \\ \uparrow\,\vdots \\ (CH_3)_2CHO\ D \end{array}\right] \rightarrow C_6H_5D + C_6H_5HgOCH(CH_3)_2. \quad (6)$$

This assumption is confirmed by the fact that the process proceeds at a temperature significantly below the temperature at which decomposition of diphenylmercury begins. The alkoxy compound formed, as we have shown using isopropylmercury isopropylate as an example ([2]), is unstable and readily dissociates into radicals:

$$C_6H_5HgOCH(CH_3)_2 \rightarrow C_6H_5Hg\cdot + (CH_3)_2CHO\cdot. \quad (7)$$

The final products of isopropoxy radicals are isopropyl alcohol and acetone.

The phenylmercury radicals that appear may decompose into mercury and phenyl radicals, or recombine. However, the insignificant yield of deuterobenzene in the reaction of diphenylmercury with isopropyl alcohol labeled in the α-position (Table 2) indicates that phenyl radicals are formed in the process in very small amounts. This also indicates that the phenylmercury radicals, apparently, interact predominantly with one another:

$$2C_6H_5Hg\cdot \rightarrow (C_6H_5)_2Hg + Hg. \qquad (8)$$

The isopropoxy radicals that appear as a result of the decomposition of phenylmercury isopropylate (equation 7) can also interact with isopropyl alcohol:

$$(CH_3)_2CHO\cdot + (CH_3)_2CHOH \rightarrow (CH_3)_2CHOH + (CH_3)_2\dot{C} - OH. \qquad (9)$$

Indeed, when the reaction was carried out in alcohol labeled in the α-position, formation of about 10% of the iso-C_3H_7OD form was observed. As already indicated, in the thermal reaction of diphenylmercury with alcohols, free phenyl radicals are hardly formed, and consequently they do not generate the radicals $(CH_3)_2\dot{C} - OH(D)$. However, when the reaction was carried out with alcohol labeled in the hydroxyl group, transfer of deuterium into the α-position of the alcohol was detected (0.9%, which corresponds to a 24% yield of the alcohol $(CH_3)_2CDOD$, calculated on the basis of the starting alcohol containing 100% deuterium). This fact indicates that $(CH_3)_2\dot{C} - OD$ radicals are formed in the reaction, the source of their generation evidently being isopropoxy radicals.

In the thermal reaction of diphenylmercury with alcohols labeled in the hydroxyl group, the isotopic varieties of diphenyl correspond to the isotopic composition of benzene (Table 2). This indicates that diphenyl is formed mainly as a result of the interaction of phenyl radicals with benzene. However, in the photolysis of diphenylmercury in isopropyl alcohol labeled in the α-position (Table 1), the diphenyl form $C_{12}H_{10}$ does not correspond to the content of the benzene variety C_6H_6 obtained. This discrepancy indicates that, in the photoreaction, diphenyl is formed predominantly as a result of dimerization of phenyl radicals.

Analysis of benzenes and diphenyls for isotopic composition was carried out by the method of low-voltage mass spectrometry [7] on an MI-1305 instrument. The content of isotopic forms was calculated from the intensities of the peaks of molecular ions, taking into account corrections for the natural abundance of the isotope C^{13} and of deuterium. The mean relative error in determining the isotopic varieties of benzene and diphenyl did not exceed 5%.

The isotopic composition of isopropyl alcohol labeled with deuterium in the α-position was determined from the intensities of the principal lines [8] with $m/e = 45$ and $m/e = 46$. The amount of deuterium in the hydroxyl group was determined from the isotopic composition of monodeuteromethane obtained by the action of the alcohol on an excess of Grignard reagent in isoamyl ether.

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