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Abstract

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REACTIONS OF ACYL PEROXIDES WITH DIETHYLMERCURY

It is known that organic peroxides and oxygen initiate many reactions of organometallic compounds. Traces of oxygen accelerate the decomposition of diisopropylmercury ([1]) and retard the thermal decomposition of tetraethyllead ([2]); a number of reactions of organometallic compounds with halogen derivatives are catalyzed by peroxides ([3]) or by oxygen ([4]), etc. To elucidate the mechanism of processes of this kind it is important to know how the peroxides themselves react with organometallic compounds. A study of the reactions of peroxide compounds with ethyl derivatives of group IV elements showed that their mechanism depends on the nature of the element forming the organoelement compound ([5]). On this basis it seemed of interest to investigate the interaction of acyl peroxides with diethylmercury, in which the central atom, by its nature, differs sharply from the group IV elements. In addition, in diethylmercury there are fewer steric hindrances to attack on the central atom, which may also impart a special character to the reaction with peroxides. So far as we know, the interaction of organomercury compounds with peroxides has not hitherto been investigated, although the initiating action of peroxides on reactions of R_2Hg with CCl_4 has been established quite clearly ([3,6]).

In order to avoid side processes, the interaction of acyl peroxides with diethylmercury was studied in the absence of solvents in a nitrogen atmosphere. The peroxides were dissolved in a tenfold molar excess of diethylmercury, and the resulting solution was heated to 70–95° until gas evolution ceased (10–12 hr). The results of the experiments are summarized in Table 1; from the data the following points deserve special attention:

1. The liberation of metallic mercury is very slight. Thus, acyl peroxides do not initiate the decomposition of diethylmercury, as occurred under the action of oxygen on dicyclohexylmercury ([7]) and diisopropylmercury ([1]).
2. Despite the comparatively high reaction temperature, at which dissociation of benzoyl and acetylbenzoyl peroxides is usually observed, the evolution of CO_2 is insignificant.
3. No appreciable amounts of esters are observed: ethyl benzoate, and also (in the case of acetylbenzoyl peroxide) ethyl acetate or methyl benzoate,

which might arise in the direct reaction of diethylmercury with the peroxides or in a chain process under the action of ethyl radicals on acyl peroxides.

4. A particularly interesting fact is the formation, in the course of the reactions, of isomeric ethylbenzoic acids in fairly high yield.

On the basis of all that has been said, it may be assumed that there is no chain free-radical process. This is confirmed by the low yield of CO_2, especially in the reaction with acetylbenzoyl peroxide. As is known, acetate radicals cannot exist as kinetically independent particles and in free-radical reactions must immediately decompose into CO and methyl radicals.

Table 1

Reactions of benzoyl peroxide (BP) and acetylbenzoyl peroxide (ABP) with diethylmercury in the absence of oxygen[1]

Reaction products[2]	Yield in moles per 1 mole of peroxide: reaction with BP	Yield in moles per 1 mole of peroxide: reaction with ABP	Reaction products	Yield in moles per 1 mole of peroxide: reaction with BP	Yield in moles per 1 mole of peroxide: reaction with ABP
CO_2	0.06	0.15	$C_6H_5COOC_2H_5$	traces	traces
Hg	0.08[3]	0.07[3]	$CH_3COOC_2H_5$	–	traces
CH_4	–	0.01	Mixture $C_2H_5HgOCOR$[4]	1.80	1.53
C_2H_6	0.67	0.68	C_2H_5HgJ[5]	1.78	1.51
C_2H_4	0.29	0.32	C_6H_5COOH[5]	1.59	0.55
n-C_4H_{10}	0.03	0.07	$C_2H_5C_6H_4COOH$[5]	0.24[6]	0.42[6]
Free acids	–	–	CH_3COOH[5]	–	0.56

Notes. 1. The reaction used 0.02 mole of peroxide and 0.20 mole of diethylmercury. 2. Gaseous mixtures were analyzed chromatographically. 3. The yield is given in gram-atoms per 1 mole of peroxide. 4. R = C_6H_5, $C_2H_5C_6H_4$, and CH_3 (for reaction with ABP). 5. The substances were obtained by treating an ethereal solution of the $C_2H_5HgOCOR$ mixture with an aqueous KJ solution. The precipitated C_2H_5HgJ was filtered off; the carboxylic acids were isolated by acidifying the mother liquor with H_2SO_4 solution and subsequently extracting with ether. Ethylmercury iodide and benzoic acid were identified by melting points and mixed-melting tests. Ethylbenzoic acids were proved by oxidation of the isolated acid mixture with $KMnO_4$ in alkaline medium. In the oxidation products, by the formation of fluorescein, *o*-phthalic acid was identified (in the reaction with BP). In the reaction with ABP, terephthalic acid was also found

among the oxidation products. Dimethyl ether, m.p. 138–139° (from ether); the mixed-melting test gives the same melting point. 6. The yield was determined by titration of a mixture of benzoic and ethylbenzoic acids.

In the processes under discussion, the most probable event is the formation of a reaction intermediate complex $[(C_2H_5)_2Hg \cdot (C_6H_5COOOCOR)]$, which, judging from the reaction products and their ratios, decomposes by two independent pathways. First, a peculiar process occurs involving entry of an ethyl group into the benzene ring of the peroxide. This reaction can be described by the following equation (for the complex with benzoyl peroxide).

$$(C_2H_5)_2Hg \cdot (C_6H_5CO_2)_2 \longrightarrow C_2H_5HgOCOC_6H_5 + \text{ethylbenzoic acid}$$
or
$$(C_2H_5)_2Hg \cdot (C_6H_5CO_2)_2 \longrightarrow C_2H_5HgOC(=O)\text{-}C_6H_4C_2H_5 + C_6H_5COOH \quad (1)$$

Second, the reaction complex may decompose with evolution of ethylene:

$$\text{cyclic complex} \longrightarrow C_2H_5HgOCOC_6H_5 + C_6H_5COOH + C_2H_4 \quad (2)$$

The cyclic transition state in equation (2) is depicted conventionally; it may equally well be represented with participation of the carbonyl oxygen atoms. Processes analogous to reaction (2) were previously observed by us in the interaction of acyl peroxides with tetraethyltin ([5]). For example:

$$\text{cyclic complex of } (C_2H_5)_3Sn \text{ with benzoyl peroxide} \longrightarrow (C_2H_5)_3SnOCOC_6H_5 + C_6H_5COOH + C_2H_4 \quad (3)$$

However, in the case of diethylmercury the free acids cannot be isolated or proved by the Chugaev–Tserevitinov method, which is readily explained—

by their interaction under the experimental conditions with diethylmercury, with the formation of ethane:

$$(C_2H_5)_2Hg + RCOOH \rightarrow C_2H_5HgOCOR + C_2H_6. \quad (4)$$

The equations presented explain the composition of the reaction products rather well. At the same time, the mechanism of ethylation of the benzene ring of the peroxides remains completely unclear (equation 1). From the literature it is known that processes of this kind are fairly widespread. Thus, in the decomposition of benzoyl peroxide, entry into the benzene ring of the radicals CCl_3 [8], CH_2COOH [9,10], C_6H_5 [10], and cyclo-C_6H_{11} [11] was observed. Decomposition of α-naphthoyl peroxide in carbon tetrachloride is accompanied by replacement of hydrogen in the 4-position of the naphthalene ring by a CCl_3 group [12].

In our case, the experimental material permits us to assert that attack on the benzene ring proceeds without the participation of kinetically independent ethyl radicals. Investigation of this interesting process is continuing.

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