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Abstract

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REACTIONS OF ACYL PEROXIDES WITH ORGANIC DERIVATIVES OF LEAD, TIN, AND SILICON

It is known that liquid-phase reactions in which homolytic cleavage of σ-bonds is observed may proceed either through the stage of an active complex or with the formation of kinetically independent particles. In a number of cases, both of these mechanisms can apparently accompany one another, which naturally is reflected in an increase in the assortment of final reaction products. It seems to us that precisely such a phenomenon is encountered in studying the interaction of benzoyl peroxide and acetylbenzoyl peroxide with organotin compounds in the absence of solvents and atmospheric oxygen.

Since the reactions under discussion (see Table 1) proceed only at elevated temperatures, it is logical to assume that they are caused by the decomposition of peroxide compounds:

$$C_6H_5COOOCOR \rightarrow C_6H_5COO\cdot + RCOO\cdot, \quad (1)$$

$$R = C_6H_5 \text{ or } CH_3\cdot;$$

$$C_6H_5COO\cdot \rightarrow C_6H_5\cdot + CO_2. \quad (2)$$

From the amount of carbon dioxide evolved, it is evident that reaction (2) does not play a significant role in the processes of interaction of benzoyl peroxide with tetraethyltin, triethyltin halides, and triethyltin benzoate (experiments 1–4).

The free benzoyloxy radicals formed react with organotin compounds. Judging from the formation of ethane, ethylene, and butane, this process amounts to displacement of ethyl radicals by benzoate radicals:

$$C_6H_5COO\cdot + (C_2H_5)_3SnX \rightarrow (C_2H_5)_2SnX(OCOC_6H_5) + C_2H_5\cdot. \quad (3)$$

Here and below X = C_2H_5, Cl, Br, C_6H_5COO. Comparison of the results obtained in experiments 1–4 shows that the nature of X has little effect on the course of reaction (3). At the same time, the product $(C_2H_5)_2SnX(OCOC_6H_5)$ cannot be isolated when X = Cl and Br. Instead, diethyl tin dibenzoate and diethyl tin dihalide were obtained, which can be explained by disproportionation of the initially formed product according to the equation:

$$2(C_2H_5)_2SnX(OCOC_6H_5) \rightarrow (C_2H_5)_2SnX_2 + (C_2H_5)_2Sn(OCOC_6H_5)_2. \quad (4)$$

The free ethyl radicals arising in reaction (3) disproportionate and, to a minor extent, dimerize.

$$2C_2H_5\cdot \rightarrow C_2H_6 + C_2H_4, \quad (5)$$

$$2C_2H_5\cdot \rightarrow n\text{-}C_4H_{10}. \quad (6)$$

As follows from the equations given above, upon decomposition of 1 mole of benzoyl peroxide, theoretically about 2 moles of a mixture of ga-

Table 1

Reaction of benzoyl peroxide (BP) and acetyl benzoyl peroxide (ABP) with organic derivatives of Pb, Sn, and Si in the absence of atmospheric oxygen

Exp. no.	Taken into the reaction, moles	Temp., °C	Duration, h	CO_2	CH_4	C_2H_6	C_2H_4	*n*-C_4H_{10}	Other products
1	0.010 BP; 0.20 $(C_2H_5)_4Sn$	95–97	16	0.20	–	0.26	0.55	0.02	0.66 $(C_2H_5)_3SnOCOC_6H_5$; 0.37 $(C_2H_5)_2Sn(OCOC_6H_5)_2$

Exp. no.	Taken into the reaction, moles	Temp., °C	Duration, h	CO_2	CH_4	C_2H_6	C_2H_4	*n*-C_4H_{10}	Other products
2	0.015 BP; 0.15 $(C_2H_5)_3SnCl$	95–97	16	0.14	–	0.45	0.37	0.01	0.76 $(C_2H_5)_2Sn(OCOC_6H_5)_2$[2]; 0.63 $(C_2H_5)_2SnCl_2$
3	0.015 BP; 0.16 $(C_2H_5)_3SnBr$	95–97	16	0.15	–	0.44	0.24	0.01	0.71 $(C_2H_5)_2Sn(OCOC_6H_5)_2$[3]; 0.50 $(C_2H_5)_2SnBr_2$
4	0.010 BP; 0.044 $(C_2H_5)_3SnOCOC_6H_5$	95–97	16	0.06	–	0.29	0.16	–	0.50 $(C_2H_5)_2Sn(OCOC_6H_5)_2$[3]; 0.29 $C_6H_5COOC_2H_5$
5	0.015 ABP; 0.23 $(C_2H_5)_4Sn$	80–97	5.5	0.61	0.48	0.13	0.54	0.02	0.42 $(C_2H_5)_3SnOCOCH_3$; 0.43 $(C_2H_5)_3SnOCOC_6H_5$
6	0.010 ABP; 0.16 $(C_2H_5)_3SnCl$	80–97	4	0.58	0.42	0.38	0.40	0.02	0.34 $(C_2H_5)_2Sn(OCOC_6H_5)_2$[3]; 0.34 $(C_2H_5)_2SnCl_2$[4]
7	0.005 BP; 0.10 $(C_2H_5)_4Pb$	80	3.5	0.04	–	0.92	0.38	0.26	0.60 $(C_2H_5)_3PbOCOC_6H_5$
8	0.010 BP; 0.17 $(C_2H_5)_4Si$	95–97	16	1.18	–	–	–	–	0.90 C_6H_6; 0.53 C_6H_5COOH; 0.33 $C_{16}H_{38}Si_2$[5]
9	0.0125 ABP; 0.20 $(C_2H_5)_4Si$	80–97	8	1.34	0.82	–	–	–	0.78 C_6H_6; 0.23 C_6H_5COOH; 0.33 $C_{16}H_{38}Si_2$[6]

Exp. no.	Taken into the reaction, moles	Temp., °C	Duration, h	CO_2	CH_4	C_2H_6	C_2H_4	*n*-C_4H_{10}	Other products
10	0.010 BP; 0.10 $(CH_3)_3SnC_6H_5$	95-97	16	0.12	–	–	–	–	1.00 C_6H_6; 0.11 C_6H_5–C_6H_5; 1.30 $(CH_3)_3SnOCOC_6H_5$[7]
11	0.015 BP; 0.20 $(C_2H_5)_3SiH$	95-97	16	0.63	–	0.07	0.08	traces	1.18 C_6H_5COOH; 0.60 $(C_2H_5)_3SiOCOC_6H_5$

Notes: 1. The gas mixtures were analyzed by the chromatographic method; the previously described solid substances were identified by their melting points and by mixed samples with pure substances. 2. M.p. 122-124° (from hexane). Found, %: C 51.80; H 5.18; Sn 27.87. $C_{18}H_{20}SnO_2$. Calculated, %: C 51.59; H 4.81; Sn 28.32. 3. M.p. 122-123°. A mixed sample with dibenzoate, obtained in an experiment with heating the peroxide decomposition products distilled off with $(C_2H_5)_3SnCl$, gave CH_3COOH and 0.39 mole of $(C_2H_5)_2SnO$. 5. B.p. 130-134° at 3 mm; n_D^{20} 1.4723. Found, %: C 67.09; H 12.99; Si 19.36; mol. wt. 281; $C_{16}H_{38}Si_2$. Calculated, %: C 67.05; H 13.36; Si 19.58. Mol. wt. 286.5. 6. B.p. 131-134° at 3 mm; n_D^{20} 1.4719. Found, %: C 67.32; H 12.86; Si 19.20. $C_{16}H_{38}Si_2$. Calculated, %: C 67.05; H 13.36; Si 19.58. 7. M.p. 129-131° (from heptane). Found, %: Sn 41.32; 41.40. $C_{10}H_{14}SnO_2$. Calculated, %: Sn 41.67.

gaseous hydrocarbons, since reactions (2) and (6) are only secondary in character. However, from Table 1 (experiments 1-4) it is evident that the total yield of gaseous hydrocarbons in no case reaches even 1 mole per mole of decomposed peroxide. Consequently, ethyl radicals participate in the formation not only of gaseous substances. It is known, for example, that they can initiate the decomposition of benzoyl peroxide. In this case ethyl benzoate should be present in the reaction mixture:

$$C_2H_5\cdot + C_6H_5COOOCOC_6H_5 \rightarrow C_6H_5COO\cdot + C_6H_5COOC_2H_5. \qquad (7)$$

Ethyl benzoate was isolated by us in fairly high yield from the products of the interaction of benzoyl peroxide with tribenzyloxytin triethylolovum [[unclear: compound name in source]] (experiment 4). In the remaining experiments, ethyl

ester of benzoic acid could not be isolated in pure form because of the closeness of the boiling points of this compound and of the initial organotin substances.

Thus, assuming a free-radical scheme of interaction, it is easy to explain the formation of all the products found. At the same time, it is admissible that ethyl benzoate is also obtained in the course of a reaction proceeding with intermediate formation of an active complex. For example:

$$(C_6H_5COO)_2 + (C_2H_5)_3SnX \longrightarrow$$

$$\begin{array}{l} (C_2H_5)_2Sn{-}X \quad CH_2CH_3 \\ \qquad\qquad\qquad\quad \vdots \\ \qquad\qquad\quad O \quad \vdots \\ \qquad\qquad\quad \| \quad \vdots \\ C_6H_5{-}C{=}O{-}O{-}O{-}C{-}C_6H_5 \\ \qquad\qquad\qquad\quad \| \\ \qquad\qquad\qquad\quad O \end{array} \longrightarrow (C_2H_5)_2SnX(OCOC_6H_5) + C_6H_5COOC_2H_5 \tag{8}$$

In order to check the reality of reaction (8), we studied the interaction of acetylbenzoyl peroxide with tetraethyltin and triethyltin chloride (experiments 5 and 6).

As is known ([1]), acetyloxy radicals are metastable. The very fact of their existence as kinetically independent particles is doubtful. In those cases where they could be formed, one practically has to deal with free methyl radicals:

$$CH_3COO\cdot \rightarrow CH_3\cdot + CO_2. \tag{9}$$

Therefore the formation of a significant amount of triethyltin acetate in experiment 5, in our opinion, may be regarded as weighty evidence for the occurrence of a reaction with intermediate formation of an active complex. On the other hand, the presence in the reaction products of CO_2, CH_4, and other gaseous hydrocarbons indicates the interaction of acetylbenzoyl peroxide with tetraethyltin and triethyltin chloride according to a free-radical scheme.

Thus, in the interaction of acyl peroxides with organotin compounds, it appears that both types of homolytic cleavage of covalent bonds must be dealt with simultaneously.

It is possible that precisely this peculiarity of the process can explain why RCOO –radicals, formed upon decomposition of peroxides, attack predominantly the Sn–C bonds of organotin compounds, whereas methyl and phenyl radicals, arising by reactions (2) and (9), abstract hydrogen from ethyl groups, being converted into methane and benzene, and do not react appreciably with the tin-carbon bonds. In those cases where the reactions proceed exclusively by a

free-radical mechanism (for example, in the interaction of acyl peroxides with tetraethylsilane), phenomena of this kind are not observed.

It follows from experiment 7 that the reaction of benzoyl peroxide with tetraethyllead is not fundamentally different from those considered above. But it should be noted that it is characterized by an almost complete absence of reaction (2) and proceeds successfully under milder temperature conditions. The reactions of acyl peroxides with tetraethylsilane proceed in a completely different way (experiments 8 and 9).

This is evidently explained by the stability of the silicon–carbon bond toward homolytic cleavage. As a result, for tetraethylsilane it is not possible to establish processes analogous to reactions (3) or (8). Judging from the absence of acetic acid in the reaction mixture in either the free or bound state, the interaction of tetraethylsilane with acetyl benzoyl peroxide proceeds only by a free-radical scheme. It is most probable that the primary act of the reactions under discussion consists in the decomposition of acyl peroxides according to equations (1), (2), and (9). The free radicals formed abstract hydrogen from tetraethylsilane molecules, with formation of benzoic acid, benzene, and methane.

Recombination of secondary radicals with one another leads to the formation of complex organosilicon compounds with two or more silicon atoms in the molecule. A complete characterization of products of this kind will be given in another paper. The simplest compound of this type, isolated in fairly high yield in experiments 8 and 9—a substance of composition $C_{16}H_{38}Si_2$, which in its properties and analysis is very close to compound (A), previously described in the literature [2]:

$$\begin{array}{c}(C_2H_5)_3SiCHCH_3\\ |\\ (C_2H_5)_3SiCHCH_3.\end{array} \qquad \text{(A)}$$

The stability of the Si–C bond toward homolytic cleavage was also established earlier in the study of the decomposition of benzoyl peroxide in trimethylphenylsilane medium [3]. It was found that in this case the benzene ring of trimethylphenylsilane is attacked. As a result, the principal silicon-containing products are isomeric trimethyldiphenylsilanes.

It has already been noted above that the reactions of similar organotin and organosilicon compounds with peroxides differ significantly from one another. It therefore seemed interesting to study the interaction of benzoyl peroxide with the organotin analogue of trimethylphenylsilane (experiment 10). It was established that it is characterized by the absence of gaseous hydrocarbons in the reaction mixture and by a very low yield of carbon dioxide.

Consequently, reaction (2) has a side character, and displacement of CH_3 radicals by benzoate radicals does not occur.

In the course of the reaction, trimethyltin benzoate is formed in high yield; its structure was confirmed by an independent synthesis:

$$(CH_3)_3SnOH + C_6H_5COOH \rightarrow (CH_3)_3SnOCOC_6H_5 + H_2O. \qquad (10)$$

This fact makes it possible to assert that in the trimethylphenyltin molecule the σ-bond located between the benzene ring and the metal atom is most susceptible to homolytic cleavage. The yield of diphenyl amounts to only 0.1 mole per mole of peroxide decomposed. This indicates the absence of analogy with the processes observed in the interaction of benzoyl peroxide with trimethylsilane.

Finally, we studied the reaction of benzoyl peroxide with triethylsilane (experiment 11). In this case, the silicon–hydrogen bond is primarily subject to homolytic cleavage. As a result, the principal silicon-containing product is triethylsilyl benzoate. In addition, ethane, ethylene, and butane are formed in rather low yield, which, apparently, is explained by the presence of processes similar in character to reaction (3). The phenomena of dimerization of secondary silicon-containing radicals, so characteristic of the interaction of $(C_2H_5)_4Si$ with peroxides, could not be observed in the case under discussion. Investigations in this field are continuing.

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