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Preliminary Communication

THE REACTION OF BENZOYL PEROXIDE WITH TRIMETHYLPHENYLTIN: A POLAR MECHANISM OF FORMATION OF TRIMETHYLTIN BENZOATE

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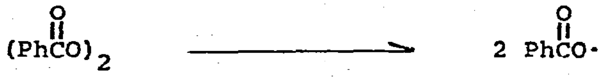
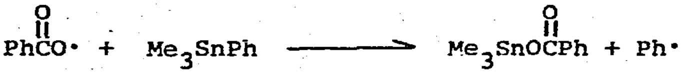
Summary

The mechanism of the reaction which gives trimethyltin benzoate by thermal decomposition of benzoyl peroxide in the presence of trimethylphenyltin was investigated. Reaction of benzoic acid, which was derived from the peroxide, with the tin compound was shown to give the benzoate.

Razuvaev et al. have reported that the thermal decomposition of benzoyl peroxide in the presence of trimethylphenyltin gives trimethyltin benzoate. Homolytic fission undoubtedly was the major pathway of the decomposition in view of the other products obtained, i.e., carbon dioxide and hydrocarbons. Accordingly, the formation of the benzoate was explained in terms of radical attack on tin (eq. 1,2).[1-3] Although there was no definite evidence for this



$$(\mathrm{Ph}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{O})_2 \longrightarrow 2\ \mathrm{Ph}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{O}\cdot \tag{1}$$



$$\mathrm{Ph}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{O}\cdot + \mathrm{Me_3SnPh} \longrightarrow \mathrm{Me_3SnO}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{Ph} + \mathrm{Ph}\cdot \tag{2}$$

mechanism, this reaction has been considered as an example of tin-carbon bond cleavage by radical attack.[4]

However, there are other possible mechanisms for the formation of trimethyltin benzoate. Thus, decomposition of benzoyl peroxide by way of coordination of the tin to the carbonyl oxygen, as in the acid-catalyzed carboxy inversion of diacyl peroxide,[5] could give the benzoate. Another possible polar process is the protodestannylation reaction of the tin compound with benzoic acid,[6,7] since the peroxide gives this acid upon thermolysis.[8]

Kinetics should answer whether the tin compound catalyzes the peroxide decomposition or not. Trapping of benzoic acid may prove the other possibility. We have investigated the mechanism of trimethyltin benzoate formation in order to obtain a better understanding of this reaction.

Rate constants for the decomposition of benzoyl peroxide were measured by iodometry in the presence or absence of additive. The results are given in Table 1.

The mode of the decomposition in the absence of an additive was not rigorously unimoleculer under the conditions used. Inhibition was observed by the addition of styrene, which in turn suggests both inhibition and acceleration of the decomposition are detectable with the peroxide concentration. The rate of the decomposition was not accelerated at all by the addition of trimethylphenyltin. These results rule out tin compound catalyzed decomposition of the peroxide.

Dicyclohexylcarbodiimide (DCC) was employed to destroy the benzoic acid produced in the reaction. In order to determine whether the added DCC or the benzoic anhydride and dicyclohexylurea which were produced affect the decomposition, the kinetics were measured in the presence of these compounds. No major effect was observed although a slight acceleration by DCC was found.

The formation of carbon dioxide was measured with or without

Table 1 Rate constants for the decomposition of benzoyl peroxide (0.01 M) at 80°C

Solvent	Additive	mole/l	$k \times 10^5 sec^{-1}$
cyclohexane	none		6.62 ± 0.59
cyclohexane	$PhCH=CH_2$	0.1	3.19 ± 0.13
cyclohexane	Me_3SnPh	0.1	4.94 ± 0.42
$CHCl_3$-cyclohexane[a)]	none		4.06 ± 0.23
$CHCl_3$-cyclohexane	Me_3SnPh	0.1	4.34 ± 0.29
$CHCl_3$-cyclohexane	DCC[b)]	0.02[c)]	5.92 ± 0.28
$CHCl_3$-cyclohexane	PhCOOCOPh	0.1	4.92 ± 0.30
$CHCl_3$-cyclohexane	DCU[d)]	0.02[c)]	3.43 ± 0.33

a) 1:1 v/v mixture. b) Dicyclohexylcarbodiimide. c) Experiments with higher concentrations could not be performed because of the limited solubility of the additive. d) N,N'-Dicyclohexylurea.

addition of DCC (under conditions similar to those used for the product analysis shown in Table 2) in order to examine the possible interception of the benzoyloxy radical by the carbodiimide.[9] The amount of the carbon dioxide was not influenced at all by the addition of DCC.* These results rule out both the possibilities of the catalyzed decomposition and the interception of the benzoyloxy radical by DCC.

Thermolysis of benzoyl peroxide was carried out in the presence of trimethylphenyltin with or without addition of DCC. Dicyclohexylurea was found as a product when DCC was present. The yield of trimethyltin benzoate was determined by integration of the PMR trimethytin signal (0.62 ppm, $CDCl_3$) relative to that of the known amounts of dichloromethane (5.21 ppm) and nitromethane (4.20 ppm)

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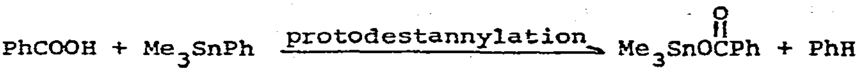
* 29 % And 28 % of CO_2 were obtained in the presence and absence of DCC, respectively.

added after evaporation of the reaction solvent. The results are shown in Table 2.

The results obtained in cyclohexane and in the mixed solvent seem to support a polar mechanism rather than radical process. Conclusive evidence was obtained by the addition of DCC. No trimethyltin benzoate was found in the product mixture. These results indicate that the tin benzoate was formed by protodestannylation of trimethylphenyltin by benzoic acid (eq. 3,4).

$$(\mathrm{Ph}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{O})_2 \xrightarrow{\text{homolysis}} 2\ \mathrm{Ph}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{O}\cdot \xrightarrow{\text{RH}} 2\ \mathrm{PhCOOH} \qquad (3)$$



$$\mathrm{PhCOOH} + \mathrm{Me_3SnPh} \xrightarrow{\text{protodestannylation}} \mathrm{Me_3SnO}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{Ph} + \mathrm{PhH} \qquad (4)$$

The process shown in reaction (4) was confirmed in a separate reaction. A mixture of benzoic acid (1 mmol) and trimethylphenyltin (2 mmol) in chloroform-cyclohexane (10 ml) was heated at 80°C for 16 hr. Trimethyltin benzoate was obtained in 47 % yield.

Table 2 Thermal decomposition of benzoyl peroxide in the presence of trimethylphenyltin at 80°C, 18 hr.[a]

Solvent	DCC mmol	$\mathrm{Me_3SnOCOPh}$, Yield (%)[b]
cyclohexane	0.0	4.4
$\mathrm{CHCl_3}$-cyclohexane[c]	0.0	13.4 (2)
$\mathrm{CHCl_3}$-cyclohexane	1.0	0.0 (2)

a) The peroxide (1 mmol) and the tin compound (2 mmol) in 10 ml of solvent. b) Parenthetical numbers indicate numbers of runs averaged, error: within 1.1 %. c) 1:1 v/v mixture.

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