The Synthesis and Properties of Tin Hydroperoxides[1]

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Trimethyltin and triphenyltin hydroperoxides have been prepared from the corresponding hydroxides and found to be reasonably stable at room temperature. Trimethyltin hydroperoxide thermally decomposes in a dilute (0.013 *M*) dioxane solution exhibiting zero-order kinetics through the initial phases of reaction with an energy of activation of 26 kcal./mole. In the latter stages of decomposition in a dilute dioxane solution or at higher concentrations (0.17 *M*), trimethyltin hydroperoxide exhibits first-order kinetics with an energy of activation (0.17 *M* solution) of 20 kcal./mole. The products in moles/mole of hydroperoxide are trimethyltin hydroxide (0.475), dimethyltin oxide (0.493), methanol (0.40), and oxygen (0.243). In acetonitrile, trimethyltin hydroperoxide also decomposes with first-order kinetics but the energy of activation is only 11 kcal./mole. The products in moles/mole of hydroperoxide are trimethyltin hydroxide (0.687), dimethyltin oxide (0.313), methanol (0.253), acetamide (0.51), and oxygen (0.302).

Investigations of the peroxides of tin have been undertaken only in the last few years. A number of papers, almost exclusively preparative in nature, have reported compounds possessing a Sn–O–O–C linkage, obtained essentially by condensation of an alkyl hydroperoxide with a tin compound.[2–5]

Bis tin peroxides are less well known. Aleksandrov and Shushunov[6–8] described bis(triethyltin) peroxide as a green oil, which decomposed completely at 0° in 1 day with an energy of activation of 14 kcal./mole. In contrast, Rieche and Dahlmann[5] have found that bis(tripropyltin) peroxide is a crystalline solid requiring several days for decomposition at room temperature. The chemical reactions of these bis peroxides have been only superficially examined.[7,8] The tin hydroperoxides have not been described until the present work.

The work reported here was undertaken to synthesize tin hydroperoxides and to investigate some of their reactions.

Experimental Section

Materials.—Acetonitrile was refluxed with phosphorus pentoxide and then distilled. Dioxane was purified by the method of Hess and Frahm.[9] Hydrogen peroxide (98%) was obtained from the FMC Corp.

Peroxide Analysis.—A sample of hydroperoxide (10 to 100 mg.) was placed in 3 *N* hydrochloric acid (20 ml.) containing potassium iodide (1 ml. of saturated solution) and titrated with sodium thiosulfate (0.1 or 0.01 *N*) using starch indicator.

Trimethyltin Hydroperoxide from Trimethyltin Hydroxide in Ether.—The use of a safety shield, goggles, etc., is recommended for this and the subsequent preparations. Trimethyltin hydroxide (2 g., 0.011 mole) was dissolved in refluxing anhydrous ether (100 ml.), the solution was cooled in an ice bath for a few seconds, and 98% hydrogen peroxide (1 ml., 0.04 mole) was added immediately. After standing at 0° (1 hr.), pure trimethyltin hydroperoxide (1.77 g., 81%), m.p. 97° dec., was isolated by filtration of the reaction mixture and washing the precipitate with ether. The infrared spectrum showed a principal peak at 3700 cm.$^{-1}$, and weaker peaks at 3650, 3550, and 1670 cm.$^{-1}$.

Anal. Calcd. for $C_3H_{10}O_2Sn$: C, 18.31; H, 5.12; active oxygen, 8.13. Found: C, 18.11; H, 4.94; active oxygen, 8.13.

Trimethyltin Hydroperoxide from Trimethyltin Hydroxide in Toluene at 0°.—To a solution of trimethyltin hydroxide (5 g., 0.028 mole) in dry toluene (200 ml.) at 0° was added 98% hydrogen peroxide (3 ml., 0.12 mole) and the mixture was kept (3 hr.) at 0° while subjected to a vacuum (0.03 mm. at best). The precipitate which formed was collected by filtration, washed with ether, and subjected to a vacuum to dry. The product (4.87 g., 90%), m.p. 97–98° dec., was kept overnight at room temperature *in vacuo* without a measurable decrease in active oxygen content (100% of theoretical).

Triphenyltin Hydroperoxide.—A solution of triphenyltin hydroxide (1 g., 0.0027 mole) in warm dry ether (100 ml.) was cooled to room temperature and 98% hydrogen peroxide (1 ml., 0.04 mole) was added immediately. Ether was removed by applying a vacuum to reduce the volume to 20 ml. In a cold room (−10°), the precipitate which formed was collected by filtration and washed with small quantities (it is quite soluble) of ether. The white crystals (0.47 g., 45%) which exploded at 75° (quite reproducible) were 96.8 to 98.1% pure by titration for active oxygen.

Anal.[10] Calcd. for $C_{18}H_{16}O_2Sn$: C, 56.4; H, 4.2; Sn, 31.0. Found: C, 55.87; H, 4.14; Sn, 31.42.

Analysis of the Products of Decomposition of Trimethyltin Hydroperoxide in Acetonitrile.—When the decomposition of the hydroperoxide in acetonitrile was complete (see Table IV for time, concentration, etc.), filtration of the reaction mixture gave dimethyltin oxide which was washed with chloroform, dried, and weighed. The infrared spectrum of the precipitate was identical with that of an authentic sample of dimethyltin oxide. The analysis indicated reasonable purity.

Anal. Calcd. for C_2H_6OSn: C, 14.6; H, 3.6; Sn, 72.1. Found: C, 13.67; H, 3.39; Sn, 73.08.

Trimethyltin hydroxide (peak at 730 cm.$^{-1}$) and acetamide (peaks at 1690 and 3500 cm.$^{-1}$) were analytically determined from the infrared spectrum of the acetonitrile filtrate. Initial identifications of these products were obtained by removing the acetonitrile by distillation and isolating pure samples of trimethyltin hydroxide and acetamide by fractional crystallization of the residue. The identities were established by comparison with authentic materials through infrared spectra and retention times by gas chromatography upon Carbowax 20M columns.

Methanol was analytically determined by gas chromatography of the acetonitrile filtrate upon a Carbowax 20M column at 80°.

Oxygen evolution was measured by collection of the evolved gas from hydroperoxide decompositions in closed systems. The gas was identified by its retention time when subjected to gas chromatography on a Molecular Sieve 5A column at 30°.

Reaction of Acetic Acid with Trimethyltin Hydroperoxide.—When acetic acid (0.092 g., 0.0015 mole) was added to trimethyltin hydroperoxide (0.30 g., 0.0015) in dioxane (10 ml.), a precipitate formed immediately. Filtration gave trimethyltin acetate (0.27 g., 0.0012 mole, 79%) identified by its melting point of 190° subl. (lit.[11] m.p. 196.5), comparison of its infrared spectrum with that of an authentic sample, and its analysis.

Anal. Calcd. for $C_5H_{12}O_2Sn$: C, 27.0; H, 5.4; Sn, 53.2. Found: C, 26.9; H, 5.38; Sn, 53.03.

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TABLE I

ZERO- AND FIRST-ORDER RATE CONSTANTS FOR THE DECOMPOSITION OF TRIMETHYLTIN HYDROPEROXIDE IN DIOXANE

Temp., °C.	Initial concn. of hydroperoxide, M	Mole % of added reagents	$10^8 k_0$, moles/ l.-sec.	% peroxide dec. with k_0 kinetics	$10^5 k_1$, sec.$^{-1}$	% peroxide dec. before k_1 kinetics
50	0.013	...	3.5	50	0.70	50
60	0.013	...	11	50	1.4	40
60	0.013	1% pyridine	10	70	2.0[a]	55
60	0.013	Glass wool	18	45	2.6[a]	50
70	0.013	...	30	60	3.6[a]	70
70	0.013	...	43	50	3.3	70
70	0.013	20% pyridine	37	30	5.3	30
80	0.013	...	140	50	9.2	65
90	0.013	...	276	50	[b]	[b]
90	0.013	20% pyridine	380	50	[b]	[b]
70	0.17	...	...	...	16	10[c]
80	0.17	...	...	...	34	10[c]
90	0.17	...	...	...	84	10[c]

[a] These figures are of very limited accuracy as they are based on only three points on a graph. [b] No portion of the curve can be considered clear first-order. [c] A short induction period is observed.

From an identical experiment in acetonitrile, trimethyltin acetate was isolated in 87% yield.

Kinetic Determinations.—Solvent was placed in a three-necked flask equipped with a reflux condenser, serum cap, and a stopper. After flushing the flask with nitrogen and equilibrating to the thermostat temperature, the hydroperoxide was added. After rapid shaking to effect solution, the first sample for titration was withdrawn within 1 min. by inserting a syringe through the serum cap. Values for zero time were obtained by extrapolation.

Results

The success in synthesis of trimethyltin hydroperoxide by partial evaporation of a mixture of toluene,

$$(CH_3)_3SnOH + H_2O_2 \rightleftharpoons (CH_3)_3SnOOH + H_2O$$

trimethyltin hydroxide, and hydrogen peroxide can be attributed to a shift in the equilibrium obtained by removing an azeotrope of toluene and water. In contrast, the preferential crystallization of the hydroperoxide from an ether solution of the tin hydroxide and hydrogen peroxide is merely a shift of equilibrium due to a favorable solubility phenomenon. Although recrystallization of the hydroperoxides is possible (trimethyltin hydroperoxide recrystallizes from tetrahydrofuran), the peroxide content generally decreases. Therefore the synthetic procedures were designed to yield essentially pure initial products.

Trimethyltin hydroperoxide is reasonably stable when pure and can be kept at room temperature for many hours without appreciable loss of peroxide content. As the triphenyltin hydroperoxide is much less stable, the studies of decomposition mechanisms were limited exclusively to the trimethyl compound. The rate of decomposition of the trimethyltin hydroperoxide is very sensitive to impurities and it is difficult to get reproducible results. As a consequence, the energies of activation are accurate only to about ±1 kcal./mole.

In a dilute (0.013 M) dioxane solution, trimethyltin hydroperoxide decomposes initially (during 50 to 60% loss of peroxide content) by a zero-order reaction (Table I, Figure 1). The rate is relatively unaffected by the addition of pyridine but is accelerated to some extent by the introduction of glass wool. Acetic acid decomposes the hydroperoxide immediately to trimethyltin acetate.

In the latter stages of the decomposition in dilute dioxane solution (last 50%) or during the entire course of reaction in more concentrated (0.17 M) dioxane solutions, the decomposition is first order with respect to the peroxide (k_1 is *ca.* 10^{-5} to 10^{-3} depending on T; E_a is 20 kcal. mole in 0.17 M solution).

The products of these decompositions in dioxane are shown in Table II. In 0.17 M solution at 70°, 0.244 mole of oxygen is evolved per mole of trimethyltin hydroperoxide.

TABLE II

MOLE PER CENT OF PRODUCTS OBTAINED FROM 0.15 M TRIMETHYLTIN HYDROPEROXIDE IN DIOXANE

Temp., °C.	Hr. for reaction	$(CH_3)_3SnOH$	$(CH_3)_2SnO$	CH_3OH
80	12	46.8	46.7	...
80	12	53.8	46.1	39.4
80	12	46.5	49.7	39.0
60	48	42.6	54.7	42.3

In acetonitrile the decomposition of trimethyltin hydroperoxide is first order (Table III, Figure 2) after an induction period. The E_a is 11 kcal./mole.

TABLE III

DECOMPOSITION OF 0.013 M TRIMETHYLTIN HYDROPEROXIDE IN ACETONITRILE

Temp., °C.	Mole % of added reagent	$10^4 k_1$, sec.$^{-1}$	Range of k_1 (% peroxide dec.)
40	...	0.52	...
50	...	1.31	25–90
50	...	0.91	35–85
50	1% acetic acid	0.92	35–75
60	...	2.21	25–85
60	20% acetic acid	2.18	15–85
60	20% pyridine	1.48	50–90
70	...	3.45	30–95
70	...	2.71	50–90
70	Decompn. products	2.63	55–95
60[a]	...	1.47	45–95

[a] 0.19 M trimethyltin hydroperoxide in acetonitrile.

The products of the decomposition in acetonitrile are shown in Table IV. The value for acetamide may be 5% too high, for some acetamide can be obtained by adding the decomposition products to fresh aceto-

TABLE IV

MOLE PER CENT OF PRODUCTS OBTAINED FROM 0.013 M TRIMETHYLTIN HYDROPEROXIDE IN ACETONITRILE

Temp., °C.	Hr. for reaction	Mole % of added reagent	$(CH_3)_3SnOH$	$(CH_3)_2SnO$	CH_3OH	$CH_3\underset{\underset{O}{\|}}{C}NH_2$
80	3	...	67.8	30.2	25.0	54.0
80	3	...	74.1	26.9	21.8	38.0
80	3	20% pyridine	70	29.4	22.1	40.6
80	3	20% methanol	68.0	35.7	26.8	56.8
60	12	...	63.6	34.3	30.7	64.2

nitrile. In 0.17 M solution at 70°, 0.302 mole of oxygen is evolved per mole of trimethyltin hydroperoxide.

The decomposition of triphenyltin hydroperoxide in acetonitrile probably follows a pattern similar to that of its trimethyl analog, for phenol (41%) and diphenyltin oxide are produced.

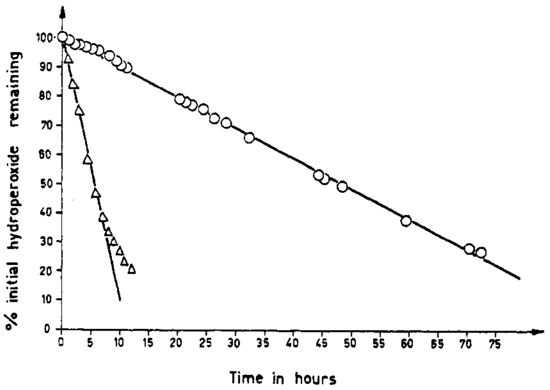

Figure 1.—Zero-order plots of the disappearance of 0.013 M trimethyltin hydroperoxide for its thermal decomposition in dioxane: ○, at 50°; and △, at 70°.

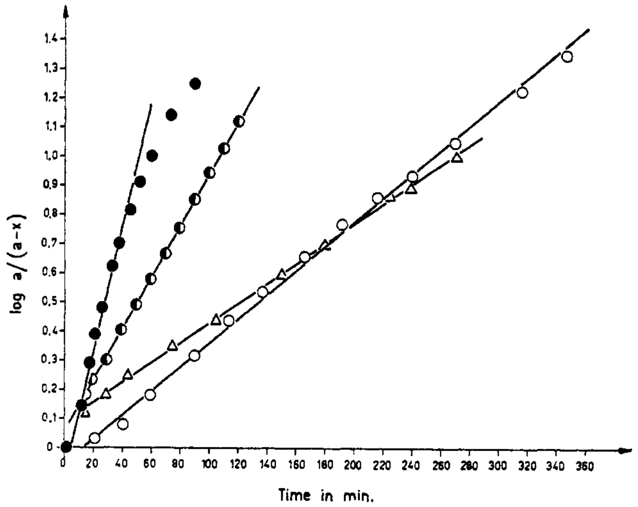

Figure 2.—First-order plots of disappearance of trimethyltin hydroperoxide in the initial concentrations and temperatures indicated: ○, 0.17 M in dioxane at 70°; ●, 0.17 M in dioxane at 90°; △, 0.013 M in acetonitrile at 50°; and ◐, 0.013 M in acetonitrile at 70°.

Discussion

The zero-order decomposition of trimethyltin hydroperoxide in dioxane may be due to impurities in the solvent or active sites on the glass surface of the containing vessel. This reasoning is substantiated by the acceleration of the zero-order rate by glass wool. It is also supported by the predominance of a first-order reaction in the latter stages of the decompositions in dilute solutions and during the major course of the decompositions in concentrated solutions, for these conditions might be expected to either remove impurities by oxidation or to deactivate active surface sites by precipitation of dimethyltin oxide.

The apparent first-order reaction in dioxane is affected by the concentration of the peroxide in regard to both the rate and energy of activation (k_{dil} at 70° = 4.2×10^{-5}, $E_{\text{a dil}}$ = 26 kcal./mole; k_{concd} at 70° = 16×10^{-5}; $E_{\text{a concd}}$ = 20 kcal./mole). This may represent an induced decomposition at high concentrations.

The products of the reaction in dioxane are of the stoichiometry shown below. Two competing reactions

$$\underset{1\text{ mole}}{(CH_3)_3SnOOH} \xrightarrow{\text{dioxane}}$$

$$\underset{0.47}{(CH_3)_3SnOH} + \underset{0.24}{O_2} + \underset{0.49}{(CH_3)_2SnO} + \underset{0.40}{CH_3OH}$$

are occurring: the first, a decomposition to oxygen and trimethyltin hydroxide; the second, a rearrangement producing dimethyltin oxide and methanol. The complex kinetic behavior and the large difference in E_a depending on solvent are an indication that the two reactions do not proceed *via* a common intermediate obtained in a rate-determining step.

The decomposition of trimethyltin hydroperoxide in acetonitrile is more rapid (k_1 at 70° = 3.4×10^{-4}) and has a lower activation energy (10.8 kcal./mole) than the first-order reaction in dioxane. The products indicate a preferential acceleration of one competing reaction. These data indicate that the trimethyltin hydroxide may be formed by an ionic reaction which

$$\underset{1\text{ mole}}{(CH_3)_3SnOOH} \xrightarrow{\text{acetonitrile}}$$

$$\underset{0.69}{(CH_3)_3SnOH} + \underset{0.30}{O_2} + \underset{0.31}{(CH_3)_2SnO} + \underset{0.25}{CH_3OH} + CH_3\underset{\underset{\underset{0.51}{O}}{\|}}{C}NH_2$$

becomes more significant in a solvent of higher polarity. Alternatively, however, the hydroperoxide may pursue an entirely different reaction path in acetonitrile involving an addition to the nitrile group. It is well known[12] that hydrogen peroxide adds to acetonitrile yielding acetamide and oxygen as ultimate products. The production of acetamide in the present case does not establish the addition mechanism, however, for acetamide could be produced by hydrolysis of an intermediate product by atmospheric moisture during the isolation of the reaction products..

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In one experiment in acetonitrile a rough rate of methanol formation was determined along with the rate of disappearance of the hydroperoxide. It was most significant that when 95% of the hydroperoxide content had disappeared, the methanol content was still 16% less than its final figure. This indicates an intermediate of some stability.

The products bear some similarity to those obtained from either triphenylsilyl hydroperoxide[13] or bis(triethyltin) peroxide.[8] The energy of activation (*ca.* 27 kcal./mole) for the first-order decomposition of the silyl hydroperoxides in most solvents is somewhat higher than that for the first-order decompositions of the tin hydroperoxide. This is reasonable in that as tin is more electropositive than silicon, it would confer a higher electron density on the attached oxygen and this generally promotes the thermal dissociation of a peroxide.[14]

$$\underset{1\ \text{mole}}{Ph_3SiOOH} \longrightarrow \underset{0.45}{Ph_3SiOH} + \underset{0.29}{Ph_2Si(OH)_2} + \text{polymer}$$

$$\underset{1\ \text{mole}}{(C_2H_5)_3SnOOSn(C_2H_5)_3} \longrightarrow \underset{1\ \text{mole}}{(C_2H_5)_3SnOC_2H_5} + \underset{1\ \text{mole}}{(C_2H_5)_2SnO}$$

Additional data are needed before mechanisms can be proposed which are not highly speculative.

Acknowledgment.—Grateful appreciation is expressed to Dr. G. E. Corbett for isolating the first sample of trimethyltin hydroperoxide.

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The Decomposition of Silyl Hydroperoxides[1]

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The thermal decomposition of triphenylsilyl hydroperoxide in anisole, methyl benzoate, nitrobenzene, and *o*-dichlorobenzene is first order and has an energy of activation of 22 to 27 kcal./mole. The reaction is complex; for example, in anisole it produces triphenylsilanol, diphenylsilanediol, phenol, and small quantities of *p*-hydroxyanisole. Triphenylsilyl, methyldiphenylsilyl, and tribenzylsilyl hydroperoxides all thermally decompose in *o*-dichlorobenzene with similar rates and almost identical energies of activation (26.7 ± 0.4 kcal./mole). The effect of the substituent group attached to silicon is therefore small. The decomposition of triphenylsilyl hydroperoxide is unaffected by acid but is accelerated by base. The base-catalyzed reaction is zero order with respect to the peroxide and has an energy of activation of 11.8 kcal./mole. Irradiation with ultraviolet light markedly accelerates the decomposition of triphenylsilyl hydroperoxide and the kinetics remain first order.

In a previous paper[2] the syntheses of several stable silyl hydroperoxides have been reported. The only other silyl hydroperoxide in the literature[3] (trimethylsilyl hydroperoxide) was described as an oil which decomposed at 0° to hydrogen peroxide and the bissilyl peroxide. No additional experiments have been performed with it.

Similarly, very little is known about the decomposition of bissilyl peroxides and the published papers[2–8] are almost exclusively preparative in nature. The only detailed study of the decomposition of a related compound concerns *t*-butyl trimethylsilyl peroxide. Hiatt[9] found that it produced acetone, *t*-butyl alcohol, and hexamethyldisiloxane by a first-order reaction sensitive to the nature of the solvent as well as to acid and base catalysis. The energy of activation was 41 kcal./mole.

The present work was undertaken to study the decomposition of silyl hydroperoxides with regard to the products formed and the kinetic behavior.

Experimental Section

Thermal Decomposition of Triphenylsilyl Hydroperoxide in Anisole.—A solution of triphenylsilyl hydroperoxide[2] (8 g., 0.0274 mole) in anisole (200 ml.) was refluxed for 12 hr. The anisole was distilled under reduced pressure (1 mm.) and the residue was dissolved in hot petroleum ether (b.p. 30–60°). Chilling the petroleum ether solution precipitated triphenylsilanol (2.3 g., 0.0083 mole), m.p. 148–152° (lit.[10] m.p. 150–152°), which was collected by filtration. The infrared spectrum was identical with that of an authentic sample. The petroleum ether filtrate was extracted with aqueous potassium hydroxide (40 ml., 1 *N*), and acidification of the aqueous extract deposited diphenylsilanediol (1.7 g., 0.0072 mole), m.p. 170–171°, which was identified by comparison of its infrared spectrum to that of an authentic sample. The acidified aqueous filtrate, after evaporation to dryness and high-vacuum distillation of the residue, gave *p*-hydroxyanisole (0.3 g., 0.0024 mole), identified as its aryloxyacetic acid derivative. From the remaining petroleum ether solution was isolated additional triphenylsilanol (1.1 g., 0.004 mole) and 2.3 g. of unidentified tar.

Thermal Decomposition of Triphenylsilyl Hydroperoxide in Dibutyl Phthalate.—A solution of triphenylsilyl hydroperoxide (4 g., 0.0137 mole) in dibutyl phthalate (100 ml.) was heated to 160° under a stream of nitrogen gas for 2 hr. in a distillation apparatus under vacuum (30 mm.). The distillate (30 ml.) was subjected to a vacuum (10^{-5} mm.) for 24 hr. at room temperature to sublime phenol (0.3 g., 0.0032 mole), m.p. 41–42°.

Base-Catalyzed Decomposition of Triphenylsilyl Hydroperoxide.—A solution of triphenylsilyl hydroperoxide (1 g., 0.0034 mole), triethylamine (1 ml., 0.01 mole), and ether (20 ml.) was heated on a steam bath while it was evaporated *in vacuo* to dryness, and the residue was dissolved in ether. The ether solution was washed with water and then cooled to precipitate triphenylsilanol (0.5 g., 0.0018 mole, 53%, m.p. 148–150°).

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[1] (a) Supported in part by the U. S. Army Research Office (Durham) through Grant No. DA-ARO(D)-31-124-G242 and in part by a Texaco Co. Fellowship. (b) Taken in part from the dissertation of G. Jalics, submitted in June 1964 to the Graduate School of Western Reserve University in partial fulfillment of the requirements for the degree of Doctor of Philosophy. (c) Presented in part at the 145th National Meeting of the American Chemical Society, New York, N. Y. Sept. 1963.

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