Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

PEROXIDES DERIVED FROM DIALKYLTIN DERIVATIVES

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(Received December 7th, 1971)

SUMMARY

Dialkyltin dimethoxides yield insoluble (probably polymeric) peroxides in a high state of purity when treated with 98% hydrogen peroxide. If an aldehyde or ketone is present, a peroxide of the general formula $(-O-CR'R''-O_2-SnR_2-)_n$ is obtained. These peroxides associate in solution so that molecular weights are difficult to obtain, but the materials are predominately simple heterocycles ($n=1$) although appreciable quantities of macrocycles or linear polymers ($n>1$) may be present. The benzaldehyde dibutyltin peroxide (1.0 mole) decomposes thermally to $(C_4H_9)_2SnO$ [0.84, isolated as $(C_4H_9)_2SnCl_2$)], oxygen (0.31), benzaldehyde (0.29), and benzoic acid (0.35). These peroxides decompose thermally by first-order kinetics (k_{50° is 10^{-2} to 10^{-3} sec^{-1}). E_a is 23 kcal/mole for the dibutyltin benzaldehyde peroxide, E_a is 18 kcal/mole for the valeraldehyde analogue. A good σ Hammett plot was obtained for the *para*-substituted benzaldehydes with a ρ of -0.43.

INTRODUCTION

Polymeric and cyclic silicon peroxides derived from dialkyldihalosilanes have been reported by Jenkner[1]. The low peroxidic content of these materials was attributed to molecular rearrangements leading to alkoxy structures.

Because of recent success in the synthesis of tin hydroperoxides[2], it was decided in the present work to undertake the synthesis of peroxides from dialkyltin derivatives and to determine their behavior when thermally decomposed*.

RESULTS AND DISCUSSION

Dimethyltin, diethyltin, and di-n-butyltin peroxides were obtained in high purity (98–99%) by treating the appropriate dimethoxides in dry ether with 98% hydrogen peroxide. The elemental analyses and peroxide contents correspond to the general formula $(-R_2SnOO-)_n$ and the IR and NMR spectra show that hydroxyl groups are absent. The structures may be either cyclic or linear, however, similar to the suggestions of Jenkner for the analogous silicon compounds.

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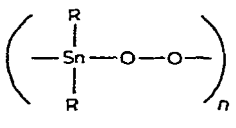
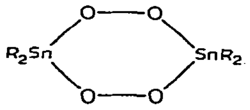
* A preliminary report of this work was presented at the Third Central Regional Meeting of the American Chemical Society at Cincinnati, Ohio, June 1971.



Linear



Cyclic
(may be larger rings)

The insolubility of the compounds prevented either molecular weight determinations or kinetic studies of their thermal decompositions. They are more stable (permitting their isolation in purities of 98 %) than their silicon analogues (isolated by Jenkner in only 38 % purity), but when stored at room temperature for thirty-eight days, the dimethyl, diethyl, and dibutyltin peroxides decreased in peroxide content to 67, 33, and 61 %, respectively, of their original values.

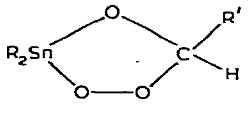
TABLE 1

PEROXIDES FROM DIALKYLTIN DIMETHOXIDES WITH CARBONYL COMPOUNDS

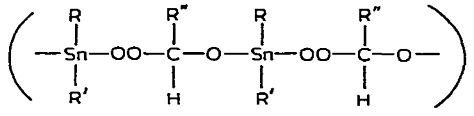
Carbonyl	*Yield* (%)	*M.p.*[a] (°C)	*Purity* (%)	*Found (calcd.)* (%)		
				C	*H*	*Sn*
With diethyltin dimethoxide						
Acetaldehyde	71	123	99	28.21 (28.50)	5.47 (5.50)	48.00 (47.00)
Benzaldehyde	68	ca. 200	106	41.47 (41.90)	5.02 (5.10)	37.77 (37.70)
With di-n-butyltin dimethoxide						
Acetaldehyde	129	125	102	38.99 (38.90)	7.14 (7.10)	38.59 (38.40)
Propionaldehyde	93	126	103	40.71 (40.90)	7.49 (7.40)	37.01 (36.80)
Benzaldehyde	79	114	110	48.34 (48.60)	6.67 (6.50)	32.11 (32.00)
p-Tolualdehyde	86	117	101	50.19 (50.04)	6.97 (6.82)	
p-Chlorobenzaldehyde	79	110–113	106	44.60 (44.40)	5.90 (5.70)	29.51 (29.30)
p-Anisaldehyde	69	103	99	47.88 (47.92)	6.59 (6.53)	
p-Nitrobenzaldehyde	83	121–123	100	43.30 (43.30)	5.66 (5.50)	28.40 (28.60)
o-Nicotinaldehyde	81	91	91	45.09 (45.20)	6.32 (6.20)	31.91 (31.90)
Terephthalic aldehyde	37	123–125	98	43.39 (43.30)	6.42 (6.30)	36.07 (35.80)
Methyl ethyl ketone	93	120	101	42.51 (42.80)	7.79 (7.70)	35.47 (35.20)
Cyclohexanone	89	133	103	46.08 (46.30)	7.59 (7.70)	32.77 (32.60)

[a] All are decomposition temperatures. There is generally only a slight change in physical appearance or sign of a gas given off at this temperature and a solid decomposition product is obtained which is high melting (over 300°) but similar in appearance to the peroxide.

The addition of 98% hydrogen peroxide to an ethereal solution of a dialkyltin dimethoxide and an aldehyde or ketone produced peroxides (Table 1) of the general formula $(-R_2Sn-O-O-CR'R''-O-)_n$. If n is one, the compounds must be cyclic (I), but if n is large, the compounds may be macrocyclic or linear polymers (II).



(I)



(II)

Molecular weights were determined to differentiate between these possible structures but variation in the molecular weight of a single sample of a peroxide was encountered with change in concentration or solvent. Association of these peroxide molecules should be possible if the tin atoms change from tetrahedral to either trigonal bipyramid or octahedral configurations through coordination with an oxygen of a second peroxide molecule.

The effect of concentration on the molecular weight of one peroxide as determined by vapor phase osmometry is shown in Table 2. Even at infinite dilution the extrapolated experimental value (ca. 480) is about 25% larger than the theoretical value (389) corresponding to a simple cyclic structure for this peroxide. This high value may represent some contamination of the simple cyclic structure with small quantities of linear or macrocyclic material.

TABLE 2

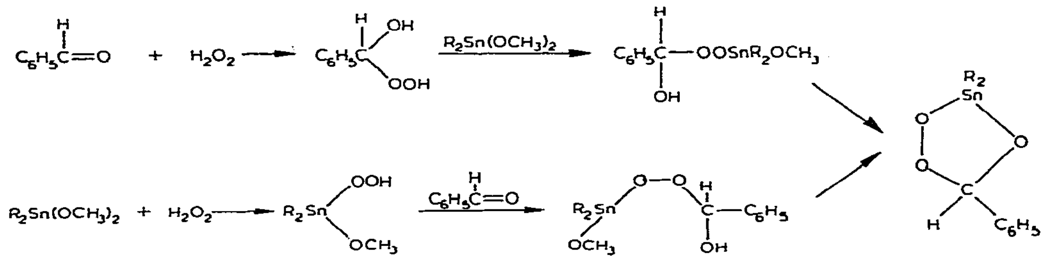
CONCENTRATION DEPENDENCE OF THE MOLECULAR WEIGHT OF $[-O-CH(CH_3)-O-O-Sn(C_4H_9)_2-]_n$ IN CHLOROFORM

Concn. (g/liter)	*Experimental molarity*	*Mol. wt.*
0		ca. 480[a]
2.07	0.0035	592
2.70	0.0043	626
4.51	0.0062	728
9.02	0.0100	902
15.34	0.0136	1130
18.20	0.0151	1210

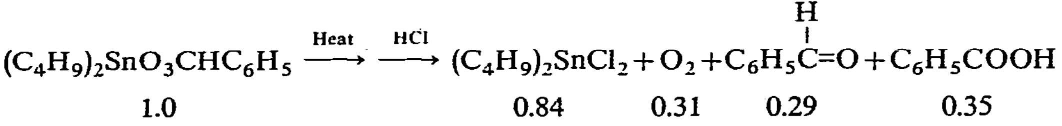
[a] Extrapolated value at infinite dilution. Theoretical mol.wt., 389 ($n = 1$).

The peroxides derived from aromatic aldehydes seem to be much less associated than the ones from aliphatic aldehydes, for even at moderate concentrations (ca. 0.27 *M*) the observed molecular weights were only about 25% larger than the calculated values for the simple cyclic structure. Thus the observed (calculated) molecular weights were: $(C_4H_9)_2SnO_2 \cdot$ *p*-anisaldehyde, 518 (401); $(C_4H_9)_2SnO_2 \cdot$ cinnamaldehyde, 477 (397); and $(C_4H_9)_2SnO_2 \cdot$ *p*-nitrobenzaldehyde, 594 (416). The relatively slightly higher molecular weight encountered with the nitro compound may not be significant but could be due to coordination of the nitro oxygens with tin atoms.

Two reaction paths are possible for the formation of the peroxide. Whether the carbonyl or the tin dimethoxide reacts first with hydrogen peroxide has not been established, but the nature of the product demands that whichever reagent reacts first, the counterpart reagent must preferentially react with the intermediate first formed. No evidence is available to choose between these alternatives or to determine the precise ionic steps.



The products of the thermal decomposition of neat dibutyltin benzaldehyde peroxide in a sealed tube were determined to be the following:



$$\underset{1.0}{(C_4H_9)_2SnO_3CHC_6H_5} \xrightarrow{\text{Heat}} \xrightarrow{\text{HCl}} \underset{0.84}{(C_4H_9)_2SnCl_2} + \underset{0.31}{O_2} + \underset{0.29}{C_6H_5\overset{H}{C}{=}O} + \underset{0.35}{C_6H_5COOH}$$

The sum of the benzoic acid and oxygen yields account for 97% of the active oxygen content of the peroxide. Most (84%) of the tin moiety has been accounted for but only 64% of the benzaldehyde fragments were identified because some tar was formed. It is possible that benzaldehyde, oxygen, and a tin moiety are the only primary products of the sealed tube decomposition, and the benzoic acid may be produced by a consecutive reaction involving the oxygen and the aldehyde.

The formation of oxygen from the thermal decomposition of a peroxide not containing the OOH group is unusual but may involve an intermediate in which the tin is in a trigonal bipyramid or tetrahedral configuration.

Kinetic studies were made of the disappearance of the active oxygen content of solutions of the various peroxides (Table 3). A plot of the log of the rate constants for the peroxides derived from aromatic aldehydes against Hammett's σ constants gives a straight line with a ρ value of -0.43. This low negative value is, of course, in agreement with a free-radical mechanism for the decomposition process with some contribution of development of a partial negative charge on the ring in the transition state.

The two energies of activation found here (18.3 and 22.9 kcal/mole) are similar to that reported for a tin hydroperoxide in dioxane[2] (20 kcal/mole).

Styrene was polymerized utilizing the dibutyltin benzaldehyde peroxide as an initiator. The ash residue (0.82%) from oxidation of the purified polymer indicated that tin was covalently attached in a ratio of 1 tin atom for 135 styrene units. The molecular weight of the polystyrene (M_w, 360,000; M_N', 135,000) was so large that tin moieties must be incorporated not only as terminal groups but also internally either in the chain or as cross linking groups.

TABLE 3

PSEUDO FIRST-ORDER RATE CONSTANTS FOR THE DISAPPEARANCE OF $(C_4H_9)_2SnO_2 \cdot RCHO$ (0.01 *M*) IN SOLUTION

RCHO of peroxide	*Solvent*	*Temp. (°C)*	$k_1 \times 10^3$ *(sec^{-1})*	E_a *(kcal/mole)*
Valeraldehyde	Toluene	50	0.44	18.3
		60	1.07	
		70	2.31	
Benzaldehyde	Chloroform	30	0.67	
		40	2.10	22.9
		50	7.3	
p-Nitrobenzaldehyde	Chloroform	50	3.50	
p-Chlorobenzaldehyde	Chloroform	50	6.0	
p-Tolualdehyde	Chloroform	50	8.1	
p-Anisaldehyde	Chloroform	50	9.3	

EXPERIMENTAL

Reaction of diethyltin dimethoxide with hydrogen peroxide

Hydrogen peroxide (2 ml, 98%) was added to a solution of diethyltin dimethoxide (1 ml, 1.48 g) in dry ether (100 ml). After the mixture had been stored overnight at −10°, it was allowed to come to room temperature and the precipitate which had formed (0.83 g, 64%) was collected by filtration and washed with ether. It melted at 97° (explosively) and was 99% pure $[(C_2H_5)_2SnO_2]_n$ by peroxide titration. (Found: C, 22.88; H, 5.00; Sn, 57.01. $C_4H_{10}O_2Sn$ calcd.: C, 22.90; H, 4.80; Sn, 56.80%.)

Reaction of dimethyltin dimethoxide with hydrogen peroxide

By a procedure identical to that described above, dimethyltin dimethoxide was converted to its peroxide, m.p. 166–167° (dec.), 98% pure by active oxygen titration. (Found: C, 12.95; H, 3.55; Sn, 66.08. $C_2H_6O_2Sn$ calcd.: C, 13.3; H, 3.3; Sn, 65.8%.)

Reaction of di-n-butyltin dimethoxide with p-nitrobenzaldehyde and hydrogen peroxide

Similarly, di-n-butyltin dimethoxide was converted in 64% yield to its peroxide, m.p. 105–108° (dec.), 99% pure by active oxygen titration. (Found: C, 36.39; H, 6.90; Sn, 44.83. $C_8H_{10}O_2Sn$ calcd.: C, 36.30; H, 6.80; Sn, 44.80%.)

Reaction of di-n-butyltin dimethoxide with p-nitrobenzaldehyde and hydrogen peroxide

Hydrogen peroxide (0.105 ml, 98%) was added to a solution of *p*-nitrobenzaldehyde (0.656 g) and di-n-butyltin dimethoxide (1 ml, 1.28 g) in dry ether (50 ml). The mixture was stored at −10° for 12 h and the ether then removed under reduced pressure. The residue yielded crystals (1.57 g, 83%) when the walls of the vessel were scratched with a stirring rod. After the product was washed with a little dry ether, its m.p. (dec.) was 121–123°.

The products of the thermal decomposition of dibutyltin benzaldehyde peroxide

The crystalline peroxide (2 g) in a nitrogen-filled sealed tube turned brown when heated at 130° for 10 min. When the tube was cooled and opened, 20 ml (0.31 mole/mole peroxide) of gas was collected in a gas burette. Gas-chromatographic analysis on an activated charcoal column proved the gas to be oxygen.

Methylene chloride (15 ml) was added to the residue and dry hydrogen chloride was bubbled through the mixture to give a clear red solution. In preliminary experiments this procedure was found to quantitatively convert $[(C_4H_9)_2SnO]_n$ to $(C_4H_9)_2SnCl_2$ which could be measured by gas chromatography using a $5' \times \frac{1}{4}''$ column at 125° of 5% SE 30 on Chromosorb W-DMCS, A/W 80/100 mesh and 2,3,5-trimethylphenol as an internal standard. The yield of $(C_4H_9)_2SnCl_2$ was 84% of theoretical.

Gas-chromatographic analysis of a second aliquot of the methylene chloride solution containing the same internal standard using a 5% FFAP column on Chromosorb G DMSC-A/W 80–100 mesh at 125° showed a 29% yield of benzaldehyde.

A second sample (0.300 g) of the peroxide was decomposed in a pressure tube by the procedure just described. The tube, after cooling, was opened and ether (70 ml) added. After filtration to remove dibutyltin oxide, the ethereal solution was extracted with three portions (40 ml each) of 5% sodium bicarbonate solution. The aqueous extract was acidified with hydrochloric acid and extracted with ether. The ether layer was dried with anhydrous magnesium sulfate and then evaporated to give benzoic acid (0.035 g, 35% yield) identified by its m.p. (122°) and its IR spectrum.

Polymerization of styrene

Freshly distilled styrene (10 g) and dibutyltin benzaldehyde peroxide (0.2 g) were placed in a pressure tube which was degassed three times and then filled with nitrogen. The tube was heated for 6 h, cooled, opened, and the contents dissolved in benzene. Addition of methanol to the benzene solution precipitated polystyrene (3 g). In a control experiment omitting the catalyst, the yield of polymer was 0.8 g. The polymer was lyophilized and a sample sent for ash analysis, yielding 0.82% residue (Galbraith Laboratories, Knoxville, Tenn.). The polymer from the control experiment gave a negligible ash analysis (0.03%).

Kinetic determinations

Analysis for the peroxide content of the solutions was performed using the method of Kokatnur and Jelling[3].

Molecular weight determinations of the peroxides

These were performed using the Mechrolab Vapor Pressure Osmometer. The polystyrene molecular weight (GPC) was supplied by Dart Industries, Inc.

ACKNOWLEDGEMENTS

This research was supported by the U.S. Army Research Office (Durham) through Grant No. DA-ARO(D)-31-124-G720 and by Dart Industries, Inc.

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