# Evidence for a Radical Chain Mechanism in the Autoxidation of Triethylbismuth

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The autoxidation of triethylbismuth in cyclohexane at 25 °C produces as major products ethanol, acetaldehyde, and a solid suggested to be $Bi_2O_3$ with oxygen atoms randomly replaced by $=CHCH_3$ or $-CH_2CH_2-$ groups. Minor products include diethyl peroxide, diethyl ether, acetic acid, and probably ethylene. The reaction is strongly inhibited by diphenylamine and a radical chain reaction is proposed to account for the observed products.

L'autoxydation du triéthyle de bismuth, dans le cyclohexane à 25 °C, conduit principalement à l'éthanol, l'acétaldéhyde et un produit solide qui serait du $Bi_2O_3$ dans lequel des atomes d'oxygène ont été remplacés au hasard par des groupes $=CHCH_3$ et $-CH_2CH_2-$. Parmi les produits formés en quantités mineures on retrouve le peroxyde d'éthyle, l'éther éthylique, l'acide acétique et probablement l'éthylène. La réaction est fortement inhibée par la diphénylamine et on croit que la réaction se produit par un mécanisme en chaîne de nature radicalique.

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## Introduction

The autoxidation of organometallic alkyls was originally thought to proceed by a nucleophilic rearrangement mechanism to yield first a peroxide, then an alkoxide (for a summary, see ref. 1), but more recent evidence (2–5) suggests that a radical chain mechanism is favored.

The autoxidation of triethylbismuth has been investigated once previously (6) and though products suggestive of a radical chain reaction were found, no attempt was made to substantiate this point. This paper reports the results of a short investigation intended to determine whether or not the reaction is in fact a radical chain and if possible to suggest a mechanism for it.

## Results and Discussion

In all cases, when the alkyl was introduced into the solvent and stirring commenced, a period of 1 to 3 min followed in which there was no apparent reaction. Immediately following this period a yellow precipitate suddenly appeared, accompanied by a rapid uptake of oxygen. The yellow compound then faded slowly until after 2 h it was entirely white. The maximum oxygen uptake of 1.5 ± 0.2 mol per mol of alkyl occurred about 5 min after injection of the alkyl; subsequently the contained gas volume increased slightly, due to evolution of gas in the reaction. Under identical conditions but with the addition of 0.1 mol% of diphenylamine, a known radical inhibitor, the oxygen uptake and solid deposition were extremely slow, with solid continuing to deposit on allowing the solution to stand for several weeks.

Results of analysis of the solid product from various reaction times are shown in Table 1. Traces of titratable peroxide were found in the product isolated after the reaction had proceeded for 5 min, but not in the product of any longer reaction period. Gas–liquid chromatography, though not absolutely reliable as an identification method, showed that ethanol, and to a lesser extent acetaldehyde, were probably the major products, together with smaller amounts of diethyl ether, diethyl peroxide, and acetic acid. All were tentatively identified by comparison with the retention times and volumes of authentic samples on two different columns.

TABLE 1. Analyses of solid autoxidation products of triethylbismuth

| Reaction time (min) | Analysis | | | | |
|---|---|---|---|---|---|
| | C,% | H,% | Bi (± 4%) | C:H | Bi:C (± 0.05) |
| 5 | 2.90 | 0.55 | 81.41 | 1:2.29 | 1:0.62 |
| 30 | 3.28 | 0.57 | 85.94 | 1:2.09 | 1:0.67 |
| 60 | 3.67 | 0.60 | 88.18 | 1:1.96 | 1:0.73 |
| 120 | 3.60 | 0.59 | 84.37 | 1:1.97 | 1:0.74 |

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[1] This work was performed in the Department of Chemistry, University of Auckland, Auckland, New Zealand.

The only gaseous product appeared to be a small amount of an unsaturated hydrocarbon.

In the earlier investigation of this reaction (6), the only ethyl containing solid product at 25 °C was EtOBiO, with Bi:C = 1:2 and C:H = 2.50, where the corresponding ratios obtained in this work are approximately 1:0.7 and 1:2.0, respectively (with the exception of the product of 5 min reaction), suggesting that intact ethyl groups are not generally present in the product. Mixture of sufficient $Bi_2O_3$ with EtOBiO would depress the Bi:C ratio to the observed figure but would not affect the C:H ratio.

Since inhibition of the reaction by diphenylamine indicates that a radical reaction does occur, and as traces of peroxide and a compound with a higher C:H ratio than 1:2 are found in a sample of the solid reaction product isolated after the reaction had proceeded for 5 min it is thought that a short-lived peroxide $Et_2BiOOEt$ is probably formed initially. Fission of the $Et_3Bi$ into radicals, attachment of oxygen to form peroxy-radicals and abstraction by them of an ethyl group from another $Et_3Bi$ molecule would achieve this. Homolytic fission of the peroxide to produce EtO· and $Et_2BiO\cdot$ radicals is likely, with the radicals then abstracting either hydrogen or ethyl groups from further $Et_3Bi$ molecules to produce ethanol and further radicals to continue the chain. Chain termination reactions involving EtO· and Et· radicals can account for the formation of diethyl peroxide, diethyl ether, and possibly acetaldehyde, though the latter may arise directly from the peroxide.

$$Et_2BiOOEt \rightarrow Et_2BiOH + MeCHO$$

A similar scheme has been proposed in the gas-phase autoxidation of triethylindium (3); there seems little reason why this should not occur in solution provided that the solvent is not involved.

As the micro-analyses indicate few intact ethyl groups in the final product (C:H ≈ 1:2.0) it is suggested that this product is a compound similar to $Bi_2O_3$ but with some of its oxygen atoms replaced by $—CH_2CH_2—$ or $>CH—CH_3$ groups and that this product eventually arises from $Et_2BiCH_2\dot{C}H_2$ or $Et_2Bi\dot{C}HCH_3$ radicals produced by hydrogen abstraction from an $Et_3Bi$ molecule.[2] Since each $Et_3Bi$ molecule reacts with 1.5 oxygen molecules the overall scheme might be represented by

$$2Et_3Bi + 3O_2 \rightarrow Bi_2O_{3/2}(C_2H_4)_{3/2} + 3EtOH + \tfrac{3}{2}CH_3CHO$$

also accounting for the fact that ethanol and acetaldehyde are the major liquid products.

Anal. Calcd. for $Bi_2O_{3/2}(C_2H_4)_{3/2}$: C, 7.44; H, 1.25; O, 4.96; Bi, 86.35; C:H = 1:2.0, and Bi:C = 1:1.5.

It is likely though that $Bi_2O_3$ is also a product (*cf.* ref. 6), and a mixture of $Bi_2O_3$ and the proposed product in, for example, a 1:1 ratio would give a solid of composition C, 3.79; H, 0.64; O, 7.58; Bi, 87.99; C:H = 1:2.0, and Bi:C = 1:0.75. These figures are reasonably close to those found in the microanalysis and suggest that such a scheme as proposed may occur.

To elucidate this mechanism further requires considerably more evidence of both kinetic and spectroscopic nature. This paper represents only an effort to suggest a reasonable mechanism based on a small amount of experimental evidence.

## Experimental

### *Preparations*

Triethylbismuth was prepared from ethylmagnesium bromide and bismuth trichloride as described by Gilman and Nelson (7). A yield of 22% was obtained. The method of transfer of the alkyl into sealed glass capsules, and other aspects of its handling in an oxygen-free atmosphere have been described by Abraham and Davies (10, and other papers in this series) for other inflammable alkyls.

Diethyl peroxide was prepared as described by Baeyer and Villiger (9). The fraction boiling at 55–75° was collected and purified as described. Gas–liquid chromatography showed two peaks, one of which corresponded to that obtained from pure diethyl ether; the other was assumed to be diethyl peroxide.

### *Analyses*

The original preparation was found to contain 70 ± 4% triethylbismuth, the remainder being a solid believed to be $Bi_2O_3$. To remove the impurities before use, a capsule was broken under cyclohexane in a small nitrogen-filled vessel fitted with a self-sealing cap. The im-

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[2] A referee has suggested that the acetic acid formed in the oxidation may be incorporated in the solid and that this possibility, together with the two outlined above, could probably be distinguished by n.m.r. Unfortunately in the author's present circumstances it is not possible to obtain further samples of the product in order to clarify this point.

purities were allowed to settle and an aliquot of the alkyl in cyclohexane withdrawn and introduced into the reaction vessel as described later. A similar aliquot was allowed to oxidize in air, the bismuth determined, and from this figure was found the amount of alkyl used and its purity (98 ± 4%). In all cases, including product analyses, the bismuth determination was made by the EDTA titration method of Cheng (8).

Peroxidic oxygen was measured by titration of the iodine liberated by the oxidation product from a solution of sodium iodide in isopropanol (11).

Liquid products were examined on a "Pye Panchromatograph" gas–liquid chromatography unit operating at ambient temperature. Columns of silicone oil (5 ft × 5 mm) and dinonyl phthalate (5 ft × 5 mm and 7 ft × 5 mm) were used with nitrogen as the carrier gas. Compounds were identified by comparison with retention times of standards, the result from the silicone oil and one of the DNP columns having to agree before an identification was confirmed.

Gases were examined with an Orsat's gas analysis apparatus, using acid mercuric sulfate and acid chromous chloride solutions as absorbents for unsaturated hydrocarbons and oxygen, respectively.

*Autoxidations*

The general method was as described by Abraham and Davies (10) except that the flask and swan-neck adaptor was replaced by a water-jacketed reaction vessel carrying a side arm with a self-sealing rubber cap. Aliquots of the alkyl in cyclohexane were injected through this after being withdrawn from the smaller vessel described earlier.

All oxidations were carried out at 25 °C using B.D.H. "Special for Spectroscopy" Grade cyclohexane as solvent. When diphenylamine was used as an inhibitor the required amount was dissolved in the solvent prior to introduction of the alkyl.

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