

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE ETHYL GASOLINE CORPORATION]

The Oxidation of Triethylbismuth

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It is generally known¹ that trialkylbismuth compounds are oxidized by air at ordinary temperatures so rapidly that they ignite spontaneously, in some cases with explosive violence.² Under these conditions the bismuth compound is probably oxidized completely to bismuth trioxide. Reports of studies on the intermediate steps or of the mechanism of such oxidations have not appeared in the literature. It was the purpose of the present work to study the oxidation of triethylbismuth under controlled conditions with the view of isolating and identifying both the intermediate and final products of oxidation, and, if possible, to determine the mechanism of such an oxidation.

Such a study has been carried out by treating triethylbismuth stepwise with oxygen under carefully controlled temperature conditions, collecting and isolating the various gaseous, liquid, and solid products formed in each step, and identifying the various products by analyses or other suitable means. Accurate weight or volume measurements were made on both the input materials and the products of oxidation, and analyses for bismuth, carbon, and hydrogen were obtained on the products. In this way it was possible to obtain complete material balances and to determine indirectly the composition of any intermediate products which were not analyzed directly.

The Stepwise Oxidation of Triethylbismuth.—

In Tables I, II and III are given the results of a typical triethylbismuth oxidation run. In the first step, an amount of oxygen corresponding to 1.3 mole per atom of bismuth reacted at -25° with the triethylbismuth; and in the second step, the solid bismuth product obtained in the previous step was allowed to react with oxygen, while raising the temperature from -40 to 25° , until reaction stopped. The final solid bismuth oxidation product was then decomposed thermally, and the products were analyzed for bismuth, carbon and hydrogen.

The products of the first step, shown in Table I, were a mixture of organic and inorganic bismuth oxides, a mixture of liquid products, and a gas.

(1) Krause and von Grosse, "Die Chemie der metallorganischen Verbindungen," Gebrüder Borntraeger, Berlin, 1937, p. 641.

(2) Gilman, Yablunsky and Svigoon, THIS JOURNAL, 61, 1170 (1939).

TABLE I
FIRST STEP OXIDATION OF TRIETHYLBISMUTH

Reactants	Grams ^a	Milli- moles	Bis- muth, milli- atoms	Et groups, milli- moles	Oxy- gen, milli- atoms
Et ₃ Bi	7.304	24.7	24.7	74.1	
O ₂ (used)	1.007	31.5			62.9
	8.311				
Products					
Solid A (Et _{1.6} BiO _{1.4}) ^b	6.820		24.6	39.0	34.0
Liquid (C _{2.0} H _{3.2} O _{0.8}) ^c	1.410				
Et ₃ Bi		0.1	0.1	0.3	
Et ₂ O		2.7		5.4	2.7
Et ₂ O ₂		10.0		20.0	20.0
EtOH		6.2		6.2	6.2
Gas (ethylene)	0.090	3.2		3.2	
	8.320		24.7	74.1	62.9

^a Determined directly by weighing or volume measurement. ^b The composition of the solid product, A, was calculated on the basis of the bismuth found by analysis, and its carbon, hydrogen, and oxygen content, obtained by subtracting the amounts of these found by analysis of the liquid and gaseous products from the total input of the elements. ^c The composition of the liquid mixture was calculated on the basis of its analysis for carbon, hydrogen, and oxygen (by difference), after first correcting for the small amount of triethylbismuth which it contained.

TABLE II
SECOND STEP OXIDATION OF TRIETHYLBISMUTH: OXIDATION OF THE SOLID, A

Reactants	Grams ^a	Milli- moles	Bis- muth, milli- atoms	Et groups, milli- moles	Oxy- gen, milli- atoms
Solid A (Et _{1.6} BiO _{1.4})	6.820 ^b		24.6 ^b	39.0 ^b	34.0 ^b
O ₂ (used)	.503				31.4
	7.323				65.4
Products					
Solid B (Et _{0.6} BiO _{1.6}) ^c	6.342		24.6	15.2	47.9
Liquid C _{2.0} H _{3.6} O _{0.8}) ^d	.904				
Et ₂ O		3.4		6.8	3.4
Et ₂ O ₂		1.1		2.1	2.1
EtOH		12.0		12.0	12.0
Gas (ethylene)	0.080	2.9		2.9	
	7.326			39.0	65.4

^a Determined directly by weighing or volume measurement. ^b From Table I. ^c The composition of the solid product, B, was calculated on the basis of the bismuth found by analysis, and its carbon, hydrogen, and oxygen content as determined by subtracting the amounts of these found by analysis in the liquid and gaseous products from the total input of these elements. ^d The composition of the liquid product was calculated from its analysis for carbon, hydrogen and oxygen (by difference).

TABLE III
THERMAL DECOMPOSITION OF THE SOLID B

Reactants	Grams ^a	Milli- moles	Bis- muth, milli- atoms	Et groups, milli- moles	Oxy- gen, milli- atoms
Solid B ^b (Et _{0.7} BiO _{1.4}) ^c	5.684		22.0	14.4	42.7
Products					
Residue	4.654		22.0	2.2	
Liquid (C ₂ H _{5.6} O _{2.8}) ^d	0.439				
EtOH		5.5		5.5	5.5
H ₂ O		10.4			10.4
Gas (CO ₂)	0.589	13.4		6.7 ^e	26.8
	5.682		22.0	14.4	42.7

^a Determined directly by weighing. ^b The small portion of the solid B which was not decomposed analyzed 540 mg. (2.6 millimoles) bismuth. ^c The composition of the solid product was calculated on the basis of the analyses of the products of decomposition. ^d The composition of the liquid product was determined from its analysis for carbon, hydrogen, and oxygen (by difference). ^e Represents ethyl groups oxidized to carbon dioxide.

The solid product was found to have the empirical formula, Et_{1.6}BiO_{1.4}. This was evidently a mixture of Et₂BiOEt, bismuth trioxide and a compound which was probably EtOBiO. The presence of Et₂BiOEt was demonstrated by actually isolating it from a similar reaction product in a later experiment; the bismuth trioxide was not isolated but its presence was indicated by the oxygen content of the mixture. The presence of EtOBiO was based on the later observation that synthetic Et₂BiOEt reacted with oxygen, cleaving two ethyl groups, and giving a product whose empirical formula approximated EtBiO₂. This product did not react further with oxygen at temperatures below 25°, and its probable composition is EtOBiO. The mixture of these three compounds which has the above empirical formula is calculated by simultaneous equations to be 54 mole % Et₂BiOEt, 26% EtOBiO, and 20% bismuth trioxide. A reasonable experimental error in the analysis would not alter these figures by more than 2%. Accepting this composition, it follows that, of the original Et-Bi bonds, 30% remained intact, 22% were oxidized to EtO-Bi, and 48% to Bi=O (or Bi-O-Bi) bonds.

The liquid product was found by analysis to have the empirical formula C_{2.0}H_{5.2}O_{0.9}. This was proved to be a mixture of diethyl peroxide, diethyl ether, and ethyl alcohol by actually isolating the three compounds, by fractionation, from the combined liquid products obtained from several preliminary runs, and by comparing the properties of the materials isolated in this way with

those recorded in the literature for the pure compounds. Figure 1 shows the distillation curve for the fractionation of the liquid mixture. The mixture of these three compounds which has the above empirical formula is calculated to be 53 mole % diethyl peroxide, 14% diethyl ether, and 33% ethyl alcohol. This composition is only approximate since it is obvious that a small experimental error in the analysis would alter the above figures greatly.

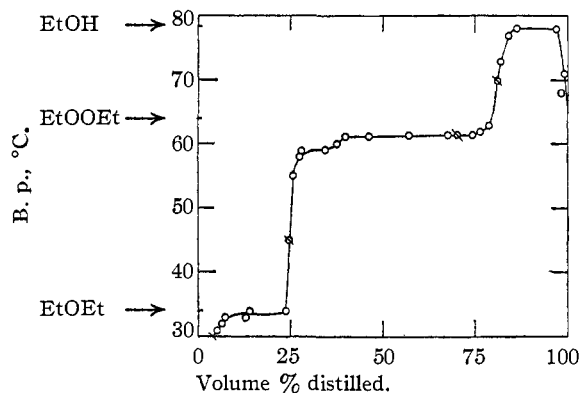


Fig. 1.—Distillation of the liquid product from the oxidation of Et₃Bi: ⊖, distillation cuts.

The small amount of gaseous product formed was identified as being mainly ethylene, together with a small amount of ethane or a hydrocarbon of higher molecular weight, by its vapor density and absorption with bromine. This was further confirmed by a combustion analysis of the combined gaseous products obtained from several preliminary runs.

The results of the second step of the oxidation, *i. e.*, the further oxidation of the solid product obtained in the first step, are shown in Table II.

The solid product, B, obtained in this second step, was found to have the empirical formula, Et_{0.6}BiO_{1.9}, and was probably a mixture of bismuth trioxide and a compound having the composition EtOBiO. That the solid product contains mainly only these two compounds is based on the observation that, of the three compounds present in the solid product of the first step of the oxidation, only Et₂BiOEt undergoes further oxidation under the conditions used. The composition of the solid product having the above empirical formula was, therefore, calculated to be a mixture of 77 mole % EtOBiO and 23% bismuth trioxide. This composition checks reasonably well with the composition of the product required if only the Et₂BiOEt of the first oxidation product were oxidized to

EtOBiO, *i. e.*, 80 mole % EtOBiO and 20% bismuth trioxide. Accepting the above composition, it follows that, of the original Et-Bi bonds, none remain intact, 79% have been oxidized to Bi=O (or Bi-O-Bi), while 21% have been oxidized to EtO-Bi bonds.

The liquid product was found by analysis to have the empirical formula $C_{2.0}H_{5.6}O_{0.8}$, and was calculated to be a mixture of 6 mole % diethyl peroxide, 21% diethyl ether and 73% ethyl alcohol.³ The gas was again assumed to be mainly ethylene.

Table III shows the results of decomposing thermally, at 350 to 450°, the solid product⁴ obtained in the second step of the oxidation. Under these conditions, the products were a residue composed mainly of metallic bismuth together with a small amount of carbon, a liquid product composed of 65 mole % water and 35% ethyl alcohol, and a gas which was identified as carbon dioxide by its vapor density and absorption on ascarite.

The Isolation and Identification of Diethylbismuth Ethoxide.—Diethylbismuth ethoxide, Et_2BiOEt , was isolated by sublimation at reduced pressure from the mixture of solid products obtained by treating triethylbismuth with a deficiency of oxygen at -60 to -50° , after distilling off the excess triethylbismuth and other volatile products. The compound obtained in this manner sublimed and condensed in the form of snow-white sword-like needles when it was heated at $70-100^\circ$ at less than 1 mm. of pressure. At 116° , it melted to a yellow liquid, and at higher temperatures, it underwent disproportionation, yielding triethylbismuth.

The identity of the compound was proved by synthesizing it in another way, namely, by the reaction of diethylbismuth bromide with sodium ethylate. The compound obtained in this way was identical in its physical appearance, and had the same chemical and physical properties as the

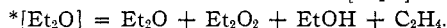
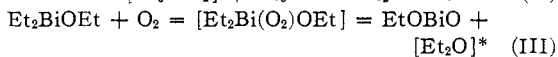
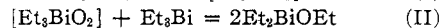
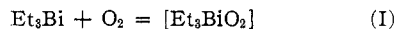
(3) It is interesting to note that the over-all composition of the liquid product obtained in the two steps of the oxidation, namely, 29 mole % diethyl peroxide, 18% diethyl ether, and 53% ethyl alcohol, checks reasonably well with the composition of the combined liquid products obtained from several previous runs which were fractionated, as estimated by the volumes and densities of the various fractions obtained, namely, 25 mole % diethyl peroxide, 18% diethyl ether and 57% ethyl alcohol.

(4) The composition of the solid product, $Et_{0.7}BiO_{1.9}$, determined on the basis of the analysis of the products of decomposition, checks within experimental error the empirical formula, $Et_{0.6}BiO_{1.9}$, of the same product, as determined in Table II on the basis of the difference between the input and output of bismuth, carbon, hydrogen and oxygen.

compound isolated by the oxidation of triethylbismuth.

Oxidation of Diethylbismuth Ethoxide.—Diethylbismuth ethoxide is relatively stable at low temperatures to further oxidation. Below 5° , it does not react with pure oxygen; and above this temperature, the oxidation must be carefully controlled. On several occasions during such oxidations, the reaction mixture flashed and exploded violently. The products of oxidation at $5-25^\circ$ are a mixture of diethyl peroxide, diethyl ether, ethyl alcohol, ethylene, and a solid whose composition approximates that of EtOBiO.

Mechanism of Oxidation.—The fact that so many products are formed in the oxidation of triethylbismuth, under the conditions studied, indicates that the mechanism of oxidation is not a simple one. No simple relationships are evident from the amounts of the various products formed. However, on the basis of the data and the results obtained in the present study, the oxidation may be postulated as taking place to a large extent in accordance with the equations



Evidence for the formation of an unstable pentavalent bismuth compound of the type, $Et_3Bi \begin{matrix} O \\ | \\ O \end{matrix}$, in accordance with eq. I, is afforded by the fact that in one experiment carried out at -60 to -50° , the reaction of oxygen with an excess of triethylbismuth gave a clear viscous liquid without the evolution of gas. When this solution was allowed to warm up slightly, after first removing the unreacted oxygen, a vigorous reaction occurred with the liberation of heat and gas, and the separation of a solid product.

The unstable intermediate, Et_3BiO_2 , may react with another molecule of triethylbismuth, in accordance with eq. II, with the formation of diethylbismuth ethoxide. This is in accord with the mechanism postulated by Johnson and Van Campen⁵ for the formation of Bu_2BOBu in the autoxidation of tributylborine. The reaction of triethylbismuth with oxygen cannot be arrested at a stage where Et_2BiOEt is the only product; even with an excess of triethylbismuth present, and with the temperature at -60° , the reaction

(5) Johnson and Van Campen, *THIS JOURNAL*, **60**, 121 (1938).

product is a mixture of all the compounds mentioned above.

The reaction of Et_2BiOEt with oxygen, in accordance with eq. III, has been demonstrated experimentally. The presence of diethyl peroxide, diethyl ether, ethyl alcohol, and ethylene in the product suggests the formation of an unstable pentavalent organic bismuth peroxide, such as $\text{Et}_2\text{Bi}(\text{O}_2)\text{OEt}$, which decomposes, giving free radicals which in turn combine to give the products listed above. Further evidence for the formation of such a peroxide is afforded by the fact that the reaction mixtures obtained during the oxidation of diethylbismuth ethoxide exploded violently on several occasions.

Compounds such as ethylbismuth oxide, EtBiO , ethylbismuth diethoxide, $\text{EtBi}(\text{OEt})_2$, and bismuth triethoxide, $\text{Bi}(\text{OEt})_3$, were not isolated; and based on the behavior of diethylbismuth ethoxide on further oxidation, it is doubtful if they are formed in appreciable amounts. Aldehydes or ethylene oxide were not detected in any of the liquid or gaseous products.

Experimental

Apparatus.—The apparatus used, illustrated in Fig. 2, was constructed of glass and consisted of the reaction vessel (A); cooling traps (B) and (C), for condensing the gaseous and volatile liquid products; a sampling trap (D) containing sample bulbs for collecting samples of the liquid products for analyses; a liquid-air trap (J) for removal of gaseous products from the circulating oxygen; a calibrated gas buret (F); a Toepler pump (G) for pumping and circulating the oxygen; and a mercury manometer (H). Connection to the oxygen supply or a vacuum pump was made at (I).

The Stepwise Oxidation of Triethylbismuth. First Step.—A 7.304-g. sample of a middle fraction of redistilled triethylbismuth was distilled into the tared reaction vessel (A). The reaction vessel was cooled to -25° by means of a dry-ice-bath, and a measured amount of oxygen from the gas buret (F) was introduced into the system and allowed to come in contact with the triethylbismuth. After a short induction period, the triethylbismuth began to absorb oxygen, slowly at first and then at an increasing rate. A white precipitate began to deposit. The reaction vessel was shaken from time to time to insure proper solution and mixing of the oxygen with the triethylbismuth. As the reaction proceeded further, the rate of oxygen absorption decreased, presumably because of dilution of the oxygen with the gaseous products and vapors of the liquid products of the reaction. As the absorption approached one mole of oxygen per atom of bismuth used, the rate became extremely slow, and, in order to facilitate further reaction, the gaseous product and part of the liquid product were distilled from the reaction mixture. These were condensed in the liquid-air trap (C) and the dry-ice trap (B), respectively. The reaction mixture remaining in the reaction vessel (A) was then treated further with oxygen.

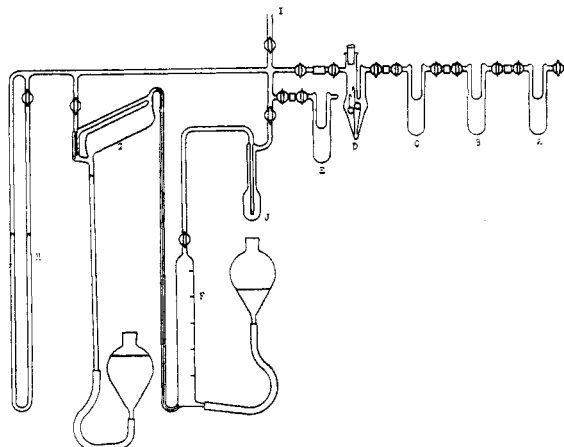


Fig. 2.—Diagram of apparatus used for the oxidation of Et_3Bi : A, reaction vessel; B, cooling trap; C, cooling trap; D, trap for sampling liquid products; E, liquid-air trap for gaseous products; F, gas buret; G, Toepler pump; H, mercury manometer; I, to oxygen supply and vacuum pump.

When approximately one mole of oxygen per atom of bismuth had reacted, the liquid products were distilled at 0° from trap A into trap B, cooled with dry-ice. Toward the end of the distillation, a bath at 50° was placed around the reaction vessel (A) and the pressure was reduced to 1 mm. in order to make sure that the last traces of triethylbismuth were distilled. The gaseous product was condensed in the liquid-air trap (C). The liquid in trap B was then treated at -25° with oxygen in order to oxidize any triethylbismuth which it contained. The gaseous product was condensed in trap D, cooled with liquid air, and the liquid was distilled into trap C where it was again treated with oxygen to oxidize the last traces of triethylbismuth. The gaseous product was then condensed in liquid-air trap (D); and the excess oxygen, after being circulated by means of the Toepler pump (G) through the liquid-air trap (J) to remove condensable gases which escaped the original condensation, was collected and measured in the gas buret (F). The gaseous product was then allowed to expand into the manometer system, where its volume was measured, and, finally, it was condensed in the liquid-air trap (E). The gas weighed 90 mg. and had a vapor density corresponding to a molecular weight of 31.4. Bromine absorption of similar gases obtained from preliminary runs indicated that it was approximately 90% ethylene. A 276-mg. sample of the combined gas from several preliminary runs analyzed 83.1% carbon, 14.8% hydrogen and 2.1% oxygen (by difference). The liquid product was distilled and condensed in the sampling trap (D) where, after being weighed (wt., 1.410 g.), it was introduced under nitrogen into sample bulbs and analyzed by combustion. It analyzed 54.88% carbon, 11.96% hydrogen and 33.16% oxygen (by difference). The weight of the solid product A, contained in the reaction vessel (A) and in traps B and C, was determined by weighing each vessel, and its composition was determined by subtracting the bismuth, carbon, hydrogen and oxygen found in the gaseous and liquid products from the total input of these elements.

Second Step.—The solid product, A, obtained in the first step of the oxidation, contained in the reaction vessel (A) and traps B and C, was treated with a measured amount of oxygen, first at -40° and, finally, at room temperature (about 25°). The absorption of oxygen was rapid at first and then slowed down progressively as the amount reacted approached 0.6 mole per atom of bismuth.

When the absorption of oxygen stopped, the liquid and gaseous products were distilled, collected, weighed, and analyzed in the manner described above. The liquid product weighed 904 mg., and analyzed 55.82% carbon, 13.07% hydrogen, and 31.11% oxygen (by difference). The gas weighed 80 mg., had a vapor density corresponding to a molecular weight of 32, and was assumed to be mainly ethylene. The solid product, B, weighed 6.342 g., and its composition was determined by subtracting the bismuth, carbon, hydrogen and oxygen found in the gaseous and liquid products from the input of these elements.

Thermal Decomposition of the Final Solid B.—The main portion of the final solid oxidation product, B (wt. 5.684 g.), which was contained in the reaction vessel (A) was heated in an evacuated system. At 350° , the material started to decompose slowly with the liberation of gas and the condensation of droplets of water in the cooler parts of the system. Above 400° , the decomposition became rapid, and at 500° was complete. The decomposition gave: 589 mg. of a gas having a vapor density corresponding to a molecular weight of 44.2, which was identified as carbon dioxide by its absorption on ascarite; 439 mg. of liquid product which analyzed 30.05% carbon, 12.13% hydrogen, and 57.82% oxygen (by difference); and 4.654 g. of residue, mainly metallic bismuth, which analyzed 98.8% bismuth and 1.2% carbon.

The small portion (658 mg.) of the final solid, B, contained in traps B and C, which was not decomposed, analyzed 540 mg. bismuth.

Fractionation of the Liquid Oxidation Product.—A 4.6-ml. sample of the liquid product which had been collected from several preliminary triethylbismuth oxidation runs was carefully fractionated through a semi-micro distillation column. The distillation curve is shown in Fig. 1 and the

properties of the various fractions collected are given in Table IV.

TABLE IV

THE DISTILLATION OF THE LIQUID OXIDATION PRODUCT

Fraction	Compound	Vol., ml.	B. p., $^{\circ}$ C. (uncor.)	d_4^{20}	n_D^{20}
1	Diethyl ether	1.10	31-45	0.72	1.354 at 17°
2	Diethyl peroxide	2.13	45-61.5	.827	1.3675 at 21°
3		0.48	61.5-70	.79	
4	Ethyl alcohol	0.90	70-78.0	.793	1.3645 at 18°

" The densities were determined by means of a graduated 1-ml. pipet.

Fraction 1 boiled mainly at $32-34^{\circ}$ and its properties correspond satisfactorily to those of diethyl ether, b. p. (760 mm.) 34.5° , d_4^{20} , 0.713, n_D^{17} 1.3542. Fraction 2 boiled mainly at $61-61.5^{\circ}$ and its properties correspond to those of diethyl peroxide,⁶ b. p. 64° , d_4^{17} 0.827, n_D^{20} 1.3700. Although the boiling point of the main portion of fraction 2 is about 2.5° below that given in the literature⁶ for the pure compound, its other properties correspond as well as could be expected, considering the small amount of material available for physical measurements. Analysis of a sample of the peroxide fraction, by reaction with an acidified potassium iodide solution containing a small amount of ferrous salt, and titration of the liberated iodine, indicated that it was 64% diethyl peroxide. The low analysis is not surprising in view of the fact that the sample was probably contaminated with ether,⁶ and that the peroxide is not decomposed completely with acidified potassium iodide solution. Fraction 4 boiled mainly at 78° and its properties correspond to those of ethyl alcohol, b. p. 78.5° , d_4^{20} , 0.789, n_D^{18} 1.3624.

The Isolation of Diethylbismuth Ethoxide.—The apparatus was the same as that used in the previous experiment with one modification; the reaction vessel (A-B) illustrated in Fig. 3, was used so that the volatile solid product could be sublimed from the non-volatile products, and transferred under nitrogen to another reaction vessel for further oxidation and analysis.

Approximately 21 g. (71 millimoles) of triethylbismuth was treated in the special reaction vessel (A-B) illustrated in Fig. 3, at -50 to -60° , with oxygen until approximately 0.2 mole per atom of bismuth had reacted. At this point, after removing the excess oxygen, it was observed that no hydrocarbon gas could be isolated from the oxygen, and that the reaction mixture was a clear viscous liquid, containing only a few crystals at the edge of the liquid. On allowing the mixture to warm up slowly in the evacuated system, there was a sudden appearance of white crystals through the liquid, accompanied by the liberation of heat and gas, and by a violent spattering action in the liquid. When the reaction mixture reached room temperature, the volatile products were distilled, oxygen was readmitted to the system, and reaction was allowed to continue at -50 to -60° until a total of about 0.3 mole of oxygen per atom of bismuth had reacted. The excess oxygen was again removed, and the reaction mixture allowed to warm to room temperature; again, spattering with the liberation of heat was noted. The volatile reaction products and the excess triethylbismuth were then removed by distillation, leaving a solid residue. The pressure within the system was re-

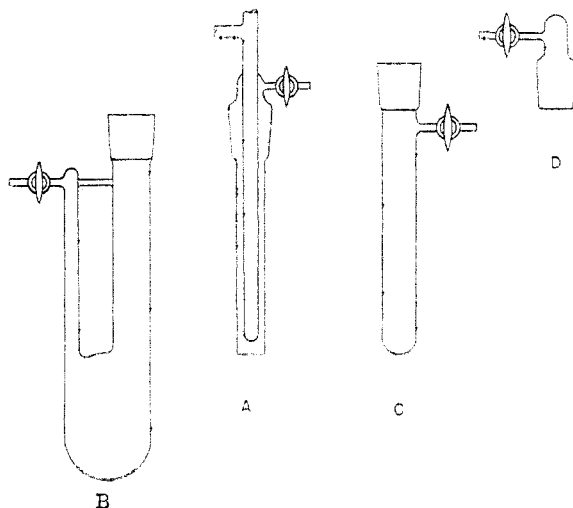


Fig. 3.—A, condenser; B, C, reaction vessels; D, stopper.

(6) Rieche, *Ber.*, **62**, 218 (1929).

duced to less than 1 mm., and a hot water-bath at 70° was placed around the reaction flask. Immediately, a volatile solid began to sublime and condense on the internal condenser in the form of snow-white sword-like crystals. The amount isolated corresponded to about 24 mole %, on the basis of the bismuth, of the solid product from which it was sublimed. The sublimate was transferred on the internal condenser (A) under nitrogen, to the reaction vessel (C) illustrated in Fig. 3, where, after being weighed, it was treated with pure oxygen at 7 to 10°. The gaseous, liquid, and solid oxidation products were collected and analyzed for bismuth, carbon, and hydrogen in the manner described above. Based on these analyses, the volatile solid product was calculated to have the empirical formula, $\text{Et}_{1.2}\text{BiO}_{1.06}$, and was probably diethylbismuth ethoxide, Et_2BiOEt .

Synthesis of Diethylbismuth Ethoxide.⁷—To 3.0 cc. (18 millimoles) of triethylbismuth in 50 cc. of hexane, contained, under nitrogen, in the reaction vessel (B) illustrated in Fig. 3, and cooled to -60°, was added dropwise 3.0 g. (19 millimoles) of bromine in 30 cc. of carbon tetrachloride which previously had been cooled to -20°. The supernatant liquid was decanted by nitrogen pressure at -40° from the white precipitated diethylbismuth bromide, and the precipitate was washed by decantation, under nitrogen, with two 50-cc. portions of hexane, cooled to -40°. Thirty cc. of absolute ethyl alcohol was then added to the solid product, and to the resulting solution was added, at room temperature, in one-half hour, a sodium ethylate solution prepared by dissolving 0.41 g. (18 milliatoms) of sodium in 20 cc. of absolute ethyl alcohol.

After allowing the reaction mixture to stand for one-half hour, most of the alcohol was distilled at room temperature under reduced pressure. The internal condenser (A), illustrated in Fig. 3, was then inserted into the reaction flask (B). On distillation at 100°, at less than 1 mm., a volatile solid product sublimed and condensed in the form of snow-white sword-like crystals. The yield was 2.75 g., 49%, based on the triethylbismuth used. *Anal.* Calcd. for Et_2BiOEt : Bi, 67.0. Found: Bi, 68.0. The compound is readily soluble in water and ethyl alcohol.

The Oxidation of Diethylbismuth Ethoxide.—A freshly sublimed sample of diethylbismuth ethoxide, prepared synthetically as described above, and contained on the internal condenser of the special reaction flask (A-C) illustrated in Fig. 3, was treated carefully with pure oxygen at 14-17°. Proper temperature control was obtained by

circulating water at the desired temperature through the internal condenser. Below 14° there was no absorption of oxygen. When no more oxygen would react at 17°, the excess oxygen was pumped off, and the gaseous, liquid, and solid products were separated and analyzed in the manner described above.

The results of the analyses showed that 466 mg. (1.50 millimoles) of diethylbismuth ethoxide reacted with 35 cc. (1.56 millimoles) of oxygen and yielded: 8.5 mg. of gas which analyzed 7.0 mg. carbon and 1.35 mg. hydrogen; 101 mg. of liquid which analyzed 58.0 mg. carbon, 13.0 mg. hydrogen, and 30 mg. oxygen (by difference); and 416 mg. of solid product. On the basis of the input of oxygen and diethylbismuth ethoxide, and the analyses of the gas and liquid products, the solid was calculated to have the empirical formula, $\text{Et}_{1.2}\text{BiO}_{1.8}$. The liquid product was calculated, on the basis of its analysis, to be a mixture of 15 mole % diethyl peroxide, 33% diethyl ether, and 52% ethyl alcohol.

In another experiment, a 2.258-g. (7.2 millimoles) sample of diethylbismuth ethoxide was treated very carefully with pure oxygen at 11-16°. When 130 ml. (5.8 millimoles) of oxygen had reacted, and while the temperature was still at 16°, the reaction mixture exploded very violently, shattering the reaction vessel to small bits.

Summary

The oxidation of triethylbismuth with pure oxygen under controlled temperature conditions has been shown to yield: a mixture of solid oxidation products, namely, bismuth oxide, diethylbismuth ethoxide, and a compound whose composition and properties correspond to EtOBiO ; a mixture of liquid products composed of diethyl peroxide, diethyl ether, and ethyl alcohol; and a gas, ethylene.

Diethylbismuth ethoxide was isolated by sublimation from a mixture of the solid oxidation products, and was identified by synthesizing it by the reaction of diethylbismuth bromide with sodium ethylate.

A possible mechanism for the oxidation of triethylbismuth, involving the formation of unstable pentavalent bismuth peroxides, has been suggested.

(7) The authors are indebted to Mr. J. Capinjola for the development of this method for the preparation of diethylbismuth ethoxide.