

RADIATION-INDUCED FORMATION OF BUTYLTIN BROMIDES

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In recent years di- and trialkyltin halides have become of increasing commercial importance. They serve primarily as intermediates in the preparation of alkyltin oxides and alkyltin carboxylates which have a wide range of industrial applications¹. The alkyltin halides are prepared in several ways². The more important methods involve the use of expensive intermediates such as Grignard reagents, organoaluminum compounds, or sodium-tin alloy. The direct reaction of tin with the higher alkyl halides can only be accomplished at high temperatures, high pressures, or both.

Kocheshkov *et al.*³⁻⁶ reported that they obtained primarily dibutyltin dibromide when a mixture of 1-bromobutane and powdered tin was irradiated. The corresponding dialkyltin dibromides were similarly obtained from ethyl bromide and 1-bromopropane with *G* values of 52 to 58 being reported for these reactions in static capsule irradiations. *G* values greater than 10³ were reported for a stirred reaction system⁶. Their work suggests a possible route to the dialkyltin halides which involves the direct reaction of tin and alkyl halide. The present program was undertaken to investigate the nature of the reactions between organic halides and tin in a radiation field. These initial studies were concerned primarily with 1-bromobutane.

EXPERIMENTAL

The reactions were conducted in a simple glass capsule which was encased in a heating mantle fitted with a thermocouple. The capsule was equipped with a reflux condenser in most experiments but in some instances the capsules were degassed and sealed. The capsule then was placed in a watertight stainless steel container and the whole unit was exposed to gamma radiation in a pool-type ⁶⁰Co source.

After irradiation, unreacted 1-bromobutane and products were separated from the tin by filtration and the tin washed with diethyl ether and acetone. The 1-bromobutane and solvents were removed by rotary evaporation and an aliquot of the products taken for analysis. The aliquot was dissolved in ethyl ether and treated with excess 3.0 *M* methylmagnesium bromide in ethyl ether to convert the butyltin bromides to the corresponding butylmethyltins. The excess methylmagnesium bromide was destroyed with a saturated solution of ammonium chloride and the salts filtered. The ether solution was then analyzed by gas-liquid chromatography. The stable butylmethyltins gave completely resolved GLC peaks. Silicone fluid (Dow Corning F60) on Chromasorb-W was used as the column packing and the temperature was programmed from 50 to 280°. The precision and accuracy was very good for this procedure⁷.

The radiation output of the source was determined using Fricke-type dosimetry. However, because of the high-*Z* materials present a significant correction was necessary to determine the dose absorbed in the sample. Photoelectric effects are usually negligible with organics but with tin they are significant. In addition, in some experiments with large samples it was noted that there was some attenuation through the sample. In our experiments the total corrections were as large as 30 %, although they varied somewhat with sample size and tin-to-1-bromobutane ratio.

Reagent-grade granular, 20-mesh Baker and Adamson tin or higher mesh tins, which were obtained by sifting reagent-grade granular, 30-mesh Mallinckrodt tin, were used as noted. These tins had a minimum assay of 99.90 %. Eastman white label 1-bromobutane was used without further purification. Gas-liquid chromatography indicated that the halide purity was greater than 99 %.

RESULTS AND DISCUSSIONS

The course and rate of the radiation-induced reaction of tin and 1-bromobutane is affected by the condition of the tin surface, the particle size of the tin, the additives present, and especially the temperature. An induction period has also been observed under all conditions investigated.

Tin surface conditioning and particle size

Early in the program it was recognized that the condition of the tin surface had a pronounced effect on the yield of products. Several chemical treatments were examined to insure a reproducibly active surface. For example, hydrogen gas was passed over the metal in an effort to reduce any oxide coating that might be present. However, this treatment partially destroyed the reactivity of the metal. The most effective method proved to be washing with dilute acid at room temperature. Dilute hydrochloric and hydrobromic acid proved to be equally effective. The surface area of the tin is reduced by the washing, presumably due to removal of a porous oxide layer. However, the reaction yields increase to a constant value with tin washed for 30 minutes. Little change in the activity of the tin was observed on further washing (Table I). In subsequent experiments all tin was washed for 30 minutes with 1.1 *N* hydrochloric acid.

TABLE I
EFFECT OF WASHING ON SURFACE AREA AND YIELD

Washing ^a period (min)	Area ^b (cm ² /g)	Absorbed dose ^c (rads)	Wt. of 1-bromobutane used (g)	Nonvolatile product (g)	G-value for <i>n</i> -Bu ₂ SnBr ₂
0	708	7.0 × 10 ⁵	21.00	0.23	4.3
15	153	1.4 × 10 ⁶	29.10	10.83	123
30	74	1.4 × 10 ⁶	24.96	13.19	149
60	55	1.4 × 10 ⁶	25.12	13.00	147
120	40	1.4 × 10 ⁶	23.15	13.68	155
240	33	1.4 × 10 ⁶	25.34	11.88	135

^a 1.1 *N* hydrochloric acid was used in washing 130 g of 35-mesh tin for each experiment.

^b Surface areas determined by Dynamic Gas Absorption Unit. ^c Dose rate was 5 × 10⁵ rads/h in each experiment. All samples irradiated at reflux temperature (101°).

The particle size of the tin also affects the yield as well as the product distribution. The yield increases regularly with increasing mesh size (decreasing particle size) over the range investigated except for the 20-mesh tin which gives a relatively high yield (Table 2). The 20-mesh tin from this particular supplier was consistently more reactive for undetermined reasons. See also Table 4. Although the absolute yields differ with tin from different suppliers, the trends in yields are consistent. Maximum yields were obtained when the tin was just covered with 1-bromobutane. However, much more halide was required to cover the 200-mesh tin than was required to cover the same weight of coarser tins. The different particle sizes also affects the product distribution. In going from coarser to finer tins the percentage of dibutyltin dibromide decreases and the percentage of tributyltin bromide increases. The percentages of the other constituents of the nonvolatile reaction product remain relatively constant (Table 2). In these reactions, the off-gases, determined by GLC, consist of butane

TABLE 2
EFFECT OF MESH SIZE ON YIELD AND PRODUCT DISTRIBUTION^a

Tin mesh size	Wt. of 1-bromobutane (g)	Nonvolatile product (g)	Distribution of product (%)				G-value for $n\text{-Bu}_2\text{SnBr}_2$
			$n\text{-Bu}_3\text{SnBr}$	$n\text{-Bu}_2\text{SnBr}_2$	$n\text{-BuSnBr}_2$	SnBr_4	
20 ^b	17.45	6.91	3.7	86.2	0.8	9.3	89
—35 ^c	15.31	4.78	2.1	89.6	0.4	7.9	66
÷35 to —48 ^c	15.58	5.39	3.2	89.0	0.7	7.1	74
÷48 to —60 ^c	12.74	11.46	8.3	81.7	0.7	9.3	145
200 ^d	38.90	21.20	11.1	78.6	0.8	9.5	215

^a All samples used 100 g of tin, which were washed with 1.1 N hydrochloric acid and were irradiated to 2×10^6 rads at reflux temperature (101°). ^b Baker and Adamson, General Chemical Division, Allied Chemical Co. ^c Separated from Mallinckrodt Chemical Works, 30-mesh tin. ^d Fisher Scientific Co.

and 1-butene in about equal amounts. As particle size decreases and the tributyltin bromide product increases, there is relatively less loss of butyl groups as gaseous products. The loss of butyl groups in this form leaves an excess of bromine atoms over butyl groups in nonvolatile product (Table 3). Since both total product and utilization of available butyl groups increase with increasing surface area (decreasing particle size), it suggests that the rate determining reactions occur entirely on the surface.

TABLE 3
EFFECT OF MESH SIZE ON BUTYL-GROUP, BROMINE-ATOM BALANCE

Tin mesh size	Bromine atoms in product/ butyl groups in product
20	1.15
—30 ÷35	1.13
—35 ÷48	1.11
—48 ÷60	1.09
200	1.06

Also, since the radiation energy is absorbed uniformly throughout the particles, increasing the surface relative to the volume should make the energy utilization more efficient, as observed.

Temperature

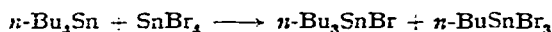
The effect of temperature on the radiation-induced formation of butyltin bromides is very pronounced. Table 4 contains typical data showing the effect of temperature at a constant dose for two different 20-mesh tins. Tin A is more reactive than Tin B as was mentioned earlier and at 80° an abnormally high percentage of butyltin tribromide was observed in the crude product. However, the general trend is the same. The reason for the differences between Tin A and Tin B is not clear at this time. The increase with temperature of the yield of the dibutyltin dibromide up to about 95° corresponds to an activation energy of approximately 35 kcal per mole. Above this temperature the activation energy becomes very small or perhaps zero.

TABLE 4
EFFECT OF TEMPERATURE ON PRODUCT YIELD AND PRODUCT DISTRIBUTION^a

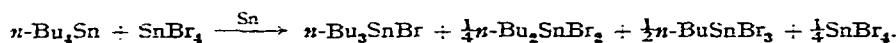
Temp. (°C)	Wt. of product (g)	Distribution of product (%)			
		<i>n</i> -Bu ₃ SnBr	<i>n</i> -Bu ₂ SnBr ₂	<i>n</i> -BuSnBr ₃	SnBr ₄
<i>Tin A</i> ^b					
75	0.544	0.0	70.4	21.6	8.0
80	1.316	0.3	76.2	14.9	8.6
85	1.595	0.4	79.6	13.7	6.3
88	1.542	0.3	74.6	15.2	9.9
93	5.770	1.9	85.8	1.1	11.2
95	8.234	2.9	84.8	0.6	11.7
98	9.725	3.8	85.9	0.8	9.5
101	10.274	3.5	83.0	1.6	11.9
<i>Tin B</i> ^c					
75	0.289	—	—	—	—
85	0.803	0.4	45.0	43.3	11.3
90	1.154	—	—	—	—
95	4.217	1.3	86.7	3.1	8.9
100	4.707	1.8	87.5	1.7	9.0

^a 130 g of tin and 22.7 ± 0.4 g 1-bromobutane were used in all experiments. All samples were irradiated to 2 × 10⁶ rads. ^b Matheson, Coleman, and Bell. Division of Matheson Company, Inc. ^c General Chemical Division, Allied Chemical.

The product distribution is also temperature-dependent. The percentage of butyltin tribromide is much higher at the lower temperatures, while the percentage of dibutyltin dibromide is lower (Table 4). However, these results are complicated by the many reactions which may occur between products. For example, we have observed the following reactions between products in refluxing 1-bromobutane:



and in the presence of tin



What seems to be a simple disproportionation reaction in refluxing 1-bromobutane is complicated by the presence of tin metal. The role of the tin metal is not understood at this time, and the possibility of many other such reactions between the different products complicates the picture even more.

One of the more striking features of the radiation-induced formation of the butyltin bromides is the induction period that has been observed with all tin samples and at all temperatures used in these experiments. The initial rate of formation of products is very low but begins to increase at about 2×10^5 rads. As the induction effect is overcome the *G*-value increases rapidly. The rate of formation of products increases continually with increasing dose, up to a dose of approximately 10^6 rads at a temperature of 101° and a dose rate of 1.82×10^5 rads/h. Fig. 1 shows the rapid increase in *G*-value during the induction period. The results shown are a composite of several series of experiments.

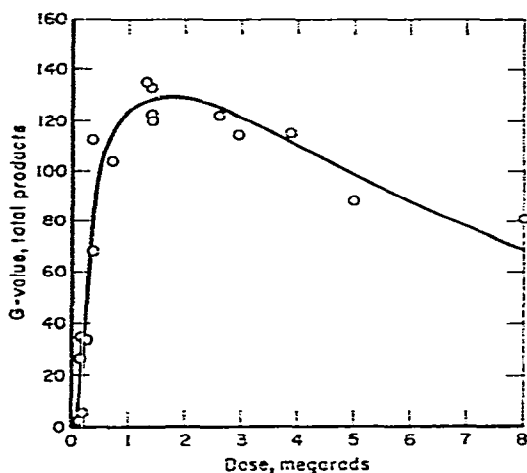


Fig. 1. *G*-value as a function of absorbed dose for butyl bromide-tin reaction system at 101° and a dose rate of 1.82×10^5 rads/h.

At least two possible causes of the induction period immediately suggest themselves. One is that the initial reactions remove some surface contaminant from the tin after which the reaction proceeds at a faster rate. Another possibility is that some intermediate must first be formed before the rapid reaction is possible. At the present time we cannot choose unequivocally between these or other explanations. However, in view of the effect of other parameters described above, the latter appears the more probable explanation.

Additives

Irradiation of alkyl halides is known to produce halogens and hydrogen halides among the reaction products. These products might be effective as surface cleaning agents or in forming necessary precursors to the alkyltin halide products. Hydrogen bromide was added to the reaction mixture prior to irradiation in some experiments. In these cases the capsule was degassed and 0.08 g of anhydrous HBr was introduced. The capsules were then sealed and irradiated. The induction period was considerably

reduced and the yields at all doses substantially increased. Although this was the expected result, it does not provide a clear-cut choice between alternate explanations of the induction period.

Several other compounds were investigated briefly as additives. The following had a promoting effect: $\text{HBr} > n\text{-BuI} > n\text{-Bu}_4\text{Sn} > \text{SnBr}_2$. On the other hand, both SnBr_4 and BrCCl_3 acted as inhibitors. Increasing the amount of HBr added can lead to the formation of relatively large amounts of SnBr_4 and ultimately reduce the reaction yield.

More recent experiments have indicated that the G -value is inversely proportional to dose rate. This very interesting effect is being investigated at present and will be reported more fully in the future. Although the G -value increases with decreasing dose rate at a fixed dose beyond the induction period, there is always some induction period to dose rates as low as 1.1×10^4 rads/h. These results seem to indicate a complex mechanism involving the formation of some necessary intermediate at the surface of the tin. Much additional work will be necessary to determine the nature of the intermediate.

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SUMMARY

Tin and 1-bromobutane can be induced by radiation to react directly. The principal product is dibutyltin dibromide. Relatively high G -values can be obtained if the tin surface is properly prepared and if the reaction is conducted at temperatures above 90° . Higher yields are obtained with tin of small particle size and a systematic variation of the product distribution with tin mesh size has been observed. Yields may be further increased by the use of HBr as an additive.

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