RADIATION-INDUCED FORMATION OF ALKYLTIN BROMIDES. PART II*

A. F. FENTIMAN, R. E. WYANT, J. L. McFARLING AND J. F. KIRCHER

Battelle Memorial Institute, Columbus Laboratories, Columbus, Ohio (U.S.A.)

(Received March 28th, 1966)

Kocheshkov *et al.*[2-5] 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 bromopropane with G values of 52 to 58 being reported for these reactions in static capsule irradiations. G values greater than 10^3 were reported for a stirred reaction system[5]. 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.

In the first paper of this series, we reported that relatively high G values could be obtained if the tin surface is properly prepared and if the reaction is conducted at temperatures above 90°. Even higher yields are obtained with tin of smaller particle size and through the use of HBr as an additive. These studies have been extended to include 1-bromopentane and other alkyl bromides, and the effect of temperature and dose rate on yield and product distribution.

EXPERIMENTAL

The reactions were conducted in glass capsules which were encased in a heating mantle fitted with a thermocouple. The containers were equipped with a reflux condenser in most experiments but in some instances the containers were degassed and sealed. The capsule was then placed in a watertight stainless steel container and the whole unit exposed to gamma radiation in a pool-type ^{60}Co source. The details of product isolation and identification are described elsewhere[1,6].

RESULTS AND DISCUSSIONS

The course and rate of the radiation-induced reaction of tin and 1-bromoalkanes are affected by temperature, radiation intensity, and total dose.

Temperature

Radiation-induced reactions of 1-bromobutane and 1-bromopentane with tin have significant activation energies. The overall activation energy for the tin/1-bromobutane system is 30.8 kcal per mole while that for the tin/1-bromopentane system is about 20 kcal per mole based on the formation of the dialkyltin dibromide. The large difference between these two very similar cases cannot be explained at the present
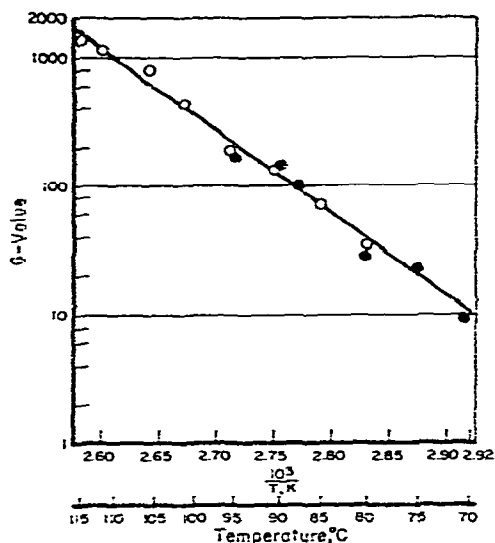
---

* For Part I see ref. 1.

Fig. 1. Activation energy for the tin/1-bromobutane system under irradiation. Data were adjusted for the difference in dose rates. The dose rate for the open-circle data was 5.75 × 10⁴ rads/h and that for the solid-circle was 2.5 × 10⁵ rads/h.
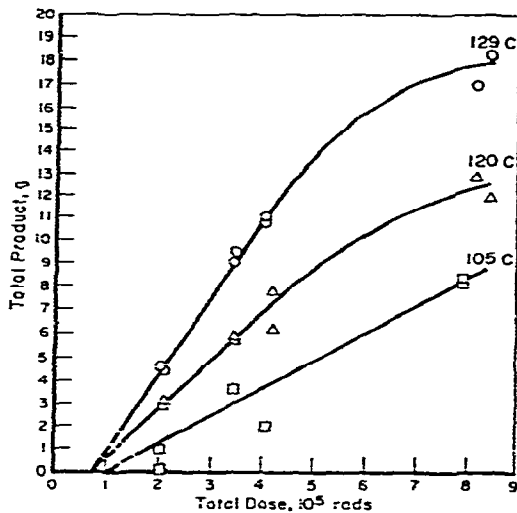
Fig. 2. Total product yield for the tin/1-bromopentane system as a function of total dose at a dose rate of 0.52 × 10⁵ rads/h and temperatures of 105, 120 and 129°.
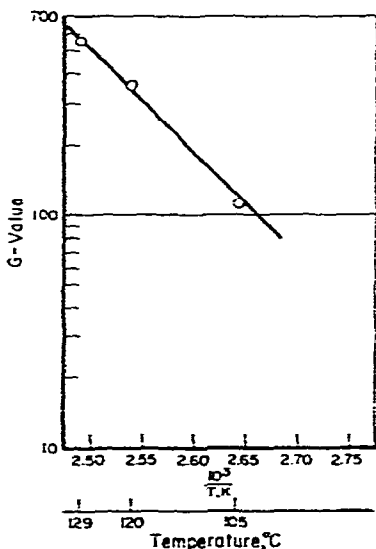

Fig. 3. Activation energy for the tin/1-bromopentane system under irradiation at a dose rate of 0.52 × 10³ rads/h measured beyond the induction region.
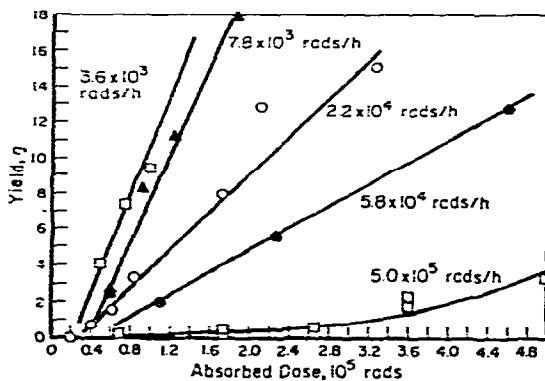
Fig. 4. Total product yield for the tin/1-bromobutane system as a function of dose at various dose rates at 101° with 130 g tin and 22.5 g 1-bromobutane.

time. Any difference in strength of the carbon–bromine bonds in the two compounds is much too small to account for the large difference in overall activation energy.

Although the tin/1-bromobutane system has always shown an induction region, this phenomenon should not influence the value of the overall activation energy if it is constant at all temperatures. Fig 1 shows the results of two separate sets of experiments performed with different samples of tin and 1-bromobutane. Data, reported previously, obtained at a dose of 2.0×10^6 rads with a dose rate of 2.50×10^5 rads/h are represented by the solid circles. The open-circle data are more recent and were obtained at total doses of 4.64×10^5 and 2.31×10^5 rads at a rate of 5.75×10^4 rads/h. The results at the higher dose rates have been corrected for the known dependency on intensity in order to make the results directly comparable. It appears, therefore, that the induction phenomenon in the tin/1-bromobutane system is constant throughout the range of temperatures and dose rates investigated.

The tin/1-bromopentane system also shows an induction effect over a range of temperatures, as shown in Fig. 2. This occurs at higher temperatures than those employed in the 1-bromobutane experiments. Fig. 3 shows the activation energy for the reaction with 1-bromopentane to be about 20 kcal per mole when measured beyond the induction region.

Dose rate

The radiation-induced reaction between 1-bromobutane and tin metal depends on the dose rate or radiation intensity. A series of experiments was performed in which the dose rate was varied by more than two orders of magnitude. At each of the five dose rates studied, a series of experiments at various total doses provided information on the reaction rate beyond the induction region. In all cases, the yield was linear with absorbed dose beyond the induction region and up to doses corresponding to conversions of about 50 %. The slopes of the linear portions of the curves shown in Fig. 4 give the yield per unit energy, or G value, at that dose rate. Fig. 5 illustrates the resulting G values *versus* the dose rate plotted logarithmically. The slope of the line is —0.5. That is, $G \simeq I^{-0.5}$, where I is the dose rate or intensity. Further reduction in the dose rate would increase the G value, *i.e.*, the yield per unit energy would increase but yield per unit time would decrease, thereby rendering experiments prohibitively long. A similar rate dependency has been recently reported at lower temperature and a narrower dose rate range by Pordeev and Pomeshchikov[7].
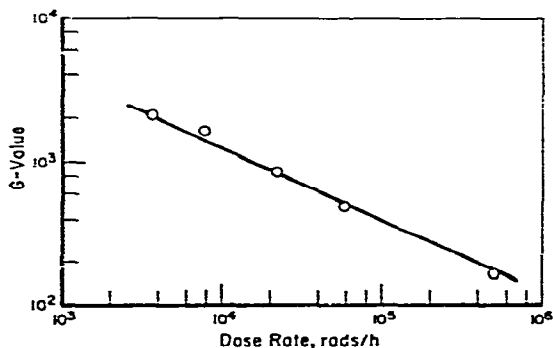

Fig. 5. G Value for total product formation at 101° and various dose rates for the tin/1-bromobutane system showing $G \simeq I^{-0.5}$ (I = dose rate).

Since G values of the order of 10^3 have been attained, the reaction must involve a long propagating-chain mechanism of some sort. The intensity dependency indicates a bimolecular termination step for the propagating chain. However, from the present data one cannot determine whether the termination reaction between active species is occurring on the tin surface or in the liquid phase.

The reaction is inhibited by oxygen as is usually the case with free-radical reactions. In the standard refluxing system used for most of this work, it is believed that little oxygen or air remains in contact with the tin or condensed butyl bromide at the reaction temperature. When the system containing oxygen is sealed, however,

TABLE I

EFFECT OF ATMOSPHERE AND TEMPERATURE ON YIELD DURING IRRADIATION OF BUTYLTIN BROMIDE PRODUCTS[a]

Atmosphere[b]	Temperature ($^\circ C$)	Yield (g)
Air	101	2.41
Nitrogen	100	2.87
Nitrogen	105	4.38
Nitrogen	110	6.20
Nitrogen	112	6.16
Nitrogen	115	7.17
Oxygen	100	0.20
Oxygen[c]	105	0.01

[a] With 130.0 g of washed 20-mesh tin and 22.6 g of distilled 1-bromobutane, all samples were irradiated at a dose rate of 8.2×10^4 rads/h. [b] Air samples were run in open capsules. Nitrogen or oxygen was added to degassed capsules which were subsequently sealed after the addition of about 3/4 atm of the gas. [c] This sample built up considerable pressure during irradiation. Other samples which contained oxygen and were irradiated at 105° or higher either exploded or leaked due to predominance of an oxidation reaction.

TABLE 2

PRODUCT DISTRIBUTION AT SEVERAL DOSES AND DOSE RATES FOR THE TIN/1-BROMOBUTANE SYSTEM[a]

Dose (10^5 rads)	Dose rate (10^5 rads/h)	Conversion (%)	Distribution of product (%)			
			Bu_3SnBr	Bu_2SnBr_2	$BuSnBr_3$	$SnBr_4$
4.86	5.20	9.1	1.1	92.9	0	6.0
8.89	1.82	16	5.4	82.3	3.3	9.0
26.9	1.82	42	3.0	83.0	7.4	6.6
56.0	1.82	61	5.0	78.7	8.6	7.7
0.66	0.31	8.0	3.5	89.9	0	6.6
2.12	0.31	41	9.6	80.1	1.2	9.1
4.86	0.31	68	10.9	77.7	5.8	5.6

[a] All samples were irradiated at reflux temperature (101°).

the desired reaction is almost completely stopped (Table 1). When oxygen is eliminated and the system sealed under nitrogen, the expected increase of yield with temperature occurs.

Product distribution

Because of the high overall activation energy, most experiments in the tin/1-bromobutane system were conducted at the boiling point of the 1-bromobutane. Under these conditions, the product distribution appears to be controlled by the degree of conversion as shown in Table 2. Various doses and dose rates were examined. At low conversions (less than 10 %), dibutyltin dibromide constitutes about 90 % of all products, regardless of the time or total dose required to reach that conversion. As the conversion increases, the percentage of dibutyltin dibromide decreases, so that at a conversion of about 60 % it becomes less than 80 % of the total. Both the tributyl and monobutyl products are increased somewhat, as if some disproportionation reaction were taking place. However, the disproportionation reaction requires irradiation and is not induced thermally. If the reaction mixture obtained at low conversions is subsequently heated for 16 h, essentially no change in composition takes place. A typical product distribution after this treatment consists of: Bu_3SnBr, 3.2 %; Bu_2SnBr_2, 88 %; $BuSnBr_3$, 0.7 %; and $SnBr_4$, 8.1 %.

Further verification of the need for irradiation to induce the observed change in product distribution was obtained from synthetic mixtures of products. A mixture simulating that found at a conversion of less than 10 % was refluxed for 32 h, about the same time as required to reach the highest conversion shown in Table 2. Although excess tin and butyl bromide were present during this treatment, the Bu_2SnBr_2 content of the mixture did not significantly change (91.9 to 91.4 %). At the same time, Bu_3SnBr increased slightly (5.5 to 7.0 %), and $BuSnBr_3$ decreased (2.6 to 0.3 %).

As reported previously[1], only at lower temperatures, *e.g.*, 70°, does $BuSnBr_3$ become an appreciable part of the total product. Higher temperatures favor the production of Bu_2SnBr_2 over other products. The large overall activation energy may be attributable to the activation energy for this product. Stannic bromide always appears among the products; in fact, it represents the second-largest product at low conversions. It would appear, therefore, that $SnBr_4$ and Bu_2SnBr_2 are the primary products at 101°. Secondary reactions in the presence of radiation produce some disproportionation giving the tributyl- and monobutyltins at higher conversions, but these products are never a major portion of the total products.

TABLE 3

EFFECT OF HEATING ON THE CRUDE PRODUCT OBTAINED FROM THE RADIATION-INDUCED REACTION OF TIN AND 1-BROMOBUTANE

Temperature (°C)	Heating period (h)	Distribution of product (%)			
		n-Bu_3SnBr	n-Bu_2SnBr_2	n-$BuSnBr_3$	$SnBr_4$
Unheated sample[a]		7.9	84.4	4.0	3.7
175	5	2.8	92.2	4.4	0.6
175	21[b]	3.7	92.1	4.2	0.0
200[c]	5	4.2	93.4	2.4	0.0
200[c]	24[d]	3.8	95.4	0.8	0.0
200	24[e]	1.2	95.9	2.9	0.0

[a] Calculations from this analysis indicate that 0.5 g of tetrabutyltin must be added to each 50.0 g of crude product to provide butyl groups so that 100 % n-Bu_2SnBr_2 could be formed. [b] Solid (1.60 g) separated before analysis. [c] This sample was heated under a nitrogen atmosphere; aliquots taken for analysis at 5 and 24 h. [d] Solid (3.74 g) separated before analysis. [e] Solid (1.35 g) separated before analysis; the solid was identified as stannous bromide.

If tetrabutyltin is added to a mixture of products, thermal disproportionation takes place, thereby increasing the dibutyltin dibromide content. About 300 g of crude product was collected from various experiments and its analysis (Table 3) is typical of the crude product obtained from the radiation-induced reaction of tin and 1-bromobutane. Calculations indicated that only a small amount of tetrabutyltin need be added to provide butyl groups so that 100 % dibutyltin dibromide can be formed. Samples of 50 g each were heated at either 175 or 200°, and aliquots were taken at different times and analyzed (Table 3). After as little as 5 h at 175°, the percentage of dibutyltin dibromide had increased from 84 to 92 %. With more drastic heating (24 h at 200°), the amount of dibutyltin dibromide could be increased to almost 96 %. The simplicity of this purification and the fact that a material with a purity greater than 95 % can be obtained is significant.

TABLE 4

YIELDS OF VARIOUS 1-BROMOALKANES RELATIVE TO THAT OF 1-BROMOBUTANE

Compound	Dose rate $(10^5\ rads/h)$	Total dose $(10^5\ rads)$	G ratio[a]
1-Bromopropane	1.1	4.86	0.075
1-Bromopentane	0.22	1.75	1.1
	1.1	4.86	1.3
1-Bromohexane	1.1	4.86	0.065
1-Bromoheptane	1.1	4.86	0.77
1-Bromooctane	1.1	4.86	0.39

[a] G value of 1-bromoalkane at its boiling point relative to that of 1-bromobutane at its boiling point when both are at the same dose rate and total dose.

Other bromoalkanes

In addition to 1-bromobutane and 1-bromopentane, several other alkyl bromides were screened. Experiments with these materials were carried out at the boiling point of the particular organic reactant as a convenient elevated temperature. No attempt was made to obtain yield-*versus*-dose curves. From Table 4 it can be seen that only 1-bromopentane gave higher yields at its boiling point than 1-bromobutane at its boiling point. Comparisons of G values relative to that for 1-bromobutane are shown at equal doses and dose rates. Although most of the alkyl bromides give yields less than that of 1-bromobutane, the yields are still significant. The G value with 1-bromobutane over the range of conditions at which comparisons were made varies from about 500 to 1000.

Since detailed studies of each compound were not made, the reaction conditions employed were probably far from being optimal. Previous screening studies indicate that 2-bromobutane and 2-bromo-2-methylpropane give G values somewhat greater than those of 1-bromobutane at a comparable dose and dose rate. This is to be expected in view of the more active bromine atom in these compounds, particularly in the case of 2-bromo-2-methylpropane.

The variations in yields among the various bromides may not reflect a large difference in G value beyond the induction region. The induction region has been present in all work with 1-bromobutane and 1-bromopentane, and it is reasonable to expect that it will be in effect with other bromides. However, it may well be different

in each case and could lead to differences of the type found. More work with the individual compounds is needed to tell whether this is, in fact, the case.

Since this is a long-chain reaction initiated by gamma radiation at moderate temperatures and it requires only simple experimental techniques, a promising new route to many alkyltin compounds is suggested.

SUMMARY

The radiation-induced reaction between tin and organic bromides was shown to give high yields of organotin products and can be made to go to completion. No thermally induced reaction occurs at the temperatures used in the radiation experiments and dialkyltin dibromides are the principal products. The main characteristics of the radiation-induced reaction are an inverse-square-root relationship between G value and radiation intensity, and a positive activation energy. G values above 10^3 are achieved, indicating a chain reaction in which chain lengths of 10^2 to 10^3 are readily attained. Such reactions were obtained with a number of alkyl bromides.

REFERENCES

1 A. F. FENTIMAN, R. E. WYANT, D. A. JEFFREY AND J. F. KIRCHER, *J. Organometal. Chem.*, 4 (1965) 302.
2 L. V. ABRAMOVA, N. I. SHEVERDINA AND K. A. KOCHESHKOV, *Dokl. Akad. Nauk SSSR*, 123 (1958) 681.
3 K. A. KOCHESHKOV, N. I. SHEVERDINA AND L. V. ABRAMOVA, *Ind. Chim. Belge, Suppl.*, 2 (1959) 331.
4 L. V. ABRAMOVA, N. I. SHEVERDINA AND K. A. KOCHESHKOV, *Tr.2 -go(Vtorogo) Ves. Seveshih, po Radiata Khim. Akad. Nauk SSSR, Otd. Khim. Nauk, Moscow,* (1960) 394–7; *Chem. Abstr.*, 58 (1963) 11391b.
5 L. V. ABRAMOVA, N. I. SHEVERDINA AND K. A. KOCHESHKOV, *Industrial Uses of Large Radiation Sources*, Int. Atomic Energy Agency, Vienna, 1 (1963) 83.
6 R. D. STEINMEYER, A. F. FENTIMAN AND E. J. KAHLER, *Anal. Chem.*, 37 (1965) 520.
7 V. V. PORDEEV AND V. D. POMESHCHIKOV, Reported at the XXth Intern. Congr. Pure Appl. Chem., Moscow, July, 1965.