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The Gamma Radiolysis of Butyl Bromides

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INTRODUCTION

The four isomeric butyl bromides constitute a series of compounds in which some effects of structure on the course of radiation-induced reactions can be observed. A study of the electron bombardment of liquid butanes (*1*) showed the formation of a rather large number of products in more or less comparable yields, as well as numerous minor products. Such a result would be expected, since it has been found (*2*, *3*) that the initial splitting of saturated hydrocarbons occurs at relatively random points in the carbon skeleton. The radiation-induced decomposition of the butyl bromides follows a simpler course, because the predominant primary effect of the radiation apparently is to break the carbon-bromine bond. There is effectively a single major reaction for each isomer, accompanied by a number of minor side reactions.

EXPERIMENTAL METHODS

Liquid samples of 1 to 2 ml were sealed in Pyrex vials and subjected to the γ-radiation from a water-shielded Co^{60} source of about 750 curies. The temperature was approximately 25°C. The dose rate, determined by ferrous sulfate dosimetry, was 3.2×10^5 r/hr.

Both commerical reagent-grade (Eastman White Label) compounds and specially purified compounds were irradiated. Each of the four commerical compounds contained a total of approximately 1% of impurities detectable by gas chromatography. Of those impurities that could reasonably be expected, saturated and unsaturated hydrocarbons, alcohols, and bromides lighter or heavier than the monobromobutanes were detectable by the gas chromatographic method used. The limit of detectability was about 0.05%. Neither HBr nor free bromine would pass through the column. Bromine was undetectable by chemical analysis, the sensitivity being estimated at about 0.01%. Titration showed traces of acid, possibly HBr, less than 0.01% in each case. It was estimated that unsaturated compounds, if any were present, totaled less than 0.1%, inasmuch as infrared spectra showed no detectable absorption characteristic of ethylenic compounds. Most of the observed impurities were appreciably more volatile than the butyl bromides.

Traces of a less volatile impurity were found in some instances. Definite identification of the impurities was not attempted.

A sample of *n*-butyl bromide was purified by fractional distillation in a dry nitrogen atmosphere. The material used boiled within about 0.2°C and contained no individual impurity in concentration great enough to be detected by the gas chromatographic analysis. Less exhaustively purified samples of the other bromides were prepared by taking the center fraction from a simple distillation under vacuum.

Samples for irradiation were prepared in three ways: (1) sealed under air, (2) degassed by freezing and pumping and sealed under vacuum, and (3) deaerated by prolonged sweeping with dry nitrogen and sealed under nitrogen. Since most of the impurities in the commercial compounds were more volatile than the butyl bromides, the last-named procedure tended to give a sample somewhat purer than the starting material. The radiation yields reported are for samples sealed under nitrogen.

Analyses were made by gas chromatography on a Burrell Kromo-Tog, Model I-1. The absorbent was dinonylphthalate on acid-washed C-22 firebrick, and the sweep gas was helium. Chromatograms were prepared at 120°C, except for *tert*-butyl bromide, which had to be run at 70°C because of significant thermal decomposition at higher temperatures.

Identification of the major volatile products was confirmed by recording infrared spectra of relatively large samples separated on the chromatographic column.

The amount of noncondensable gas formed, assumed to be hydrogen, was roughly estimated from the extent of pressure buildup in the sealed vials.

The acid formed, assumed to be HBr, was determined by titration. Sodium hydroxide in isopropyl alcohol was used to titrate the irradiated tertiary butyl bromide to avoid hydrolysis.

RESULTS

Table I gives the calculated yields of identified products, expressed as number of molecules formed per 100 ev of energy absorbed. Some uncertainty is introduced into the yield determinations by the chance that some loss of volatile products may occur in transferring samples to the gas chromatograph and by the limitations on determining the amount of products by measuring areas on the chromatograph charts. The yields for which numerical values are given, except for the dibromobutanes, are probably accurate within 10 to 20%. Dibromobutane yields are subject to more uncertainty, perhaps twice as much, because of greater difficulty encountered in making quantitative determinations of these compounds. In making the calculations, it was assumed that the bromides absorbed more energy than the aqueous dosimeter in proportion to their greater electron density. The electron density in the bromides is about 1.1 times as great as in water. Yields for the major volatile products and for the isomerization of isobutyl bromide were computed for samples receiving doses of 1.9×10^{21} ev/gm. The yields of dibromobutanes were

TABLE I

Approximate Radiation Yields of Products Identified in Irradiated Butyl Bromides

Product	*G-value of product from indicated isomer*			
	Normal	*Secondary*	*Iso-*	*Tertiary*
Hydrogen[a]	Very small	Very small	Appreciable	Appreciable
Methane[b, c]	Very small	Very small	Very small	Very small
n-Butane[c, d]	3.4	6.2	0[e]	0
Isobutylene[c, d]	0	0	6.2	9.0
n-butyl bromide[d]	—	0.9	0	0
sec-butyl bromide[d]	0.2	—	0	0
isobutyl bromide[d]	0	0	—	1.8[h]
tert-Butyl bromide[c, d]	0	0	4.5	—
1,2-dibromo-2-methylpropane[d]	0	0	2.0	3.0
1,2-dibromobutane[d]	1.0	0.7	0	0
2,3-dibromobutane[d]	$\sim$0.2[f]	1.5	0	0
HBr[g]	<0.2	<0.2	<0.2	<0.2

[a] The noncondensable gas formed is assumed to be hydrogen.

[b] Methane was not determined quantitatively, but more was produced from the branched compounds than from the straight-chain compounds.

[c] Identified by infrared spectra.

[d] Identified by chromatographic retention time.

[e] Throughout the table a "zero" yield means that the product was undetectable by the analytical method used. In most cases it may be considered that G is certainly <0.1.

[f] This product had virtually the same retention time as 2,3-dibromobutane. Its presence seems difficult to explain, however, especially since little isomerization of *n*- to *sec*-butyl bromide was detectable. The amount of it collected was insufficient for spectroscopic study.

[g] The acid formed is assumed to be HBr.

[h] The identification of this product is not conclusive.

determined in samples irradiated to 3.0×10^{21} ev/gm. Some samples were given doses of 9.5×10^{21} ev/gm, and for them the yields in isomerization of normal, secondary, and tertiary butyl bromides were estimated. These samples showed minor amounts of five to ten products, mostly more volatile than the parent compounds, that were not identified conclusively.

All results in the table are for samples sealed under nitrogen. The air- or vacuum-sealed samples apparently gave the same set of products, and the yields seemed to be at least of comparable orders of magnitude. Only a few air-saturated samples of each compound were run, however; no conclusions have been drawn about quantitative effects that oxygen may have on the yields, especially in the initial stages of the irradiation.

Yields for the reagent-grade commercial compounds and for the more highly

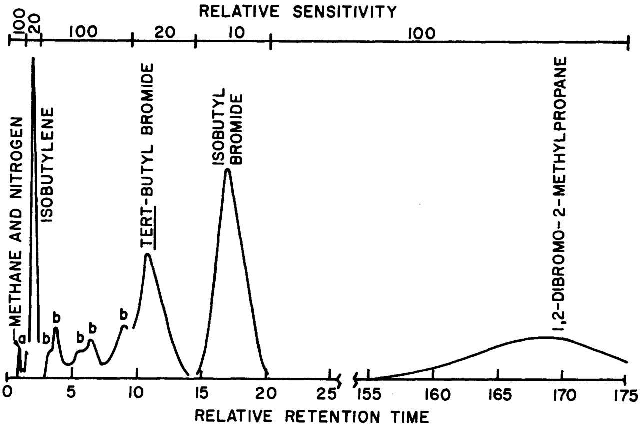

FIG. 1. Gas chromatogram of isobutyl bromide irradiated to a dose of 9.5 × 10^{21} ev/gm. (*a*) The minor peaks in this region are probably C_2 and C_3 hydrocarbons. (*b*) Products of thermal decomposition of *tert*-butyl bromide. There may also be minor radiation products in this region.

purified samples differed by less than the estimated experimental error. The impurities may have more significant effects during the initial stages of the radiation-induced reactions than on the ultimate results for samples given these comparatively high doses.

The chromatogram for irradiated isobutyl bromide is shown in Fig. 1. It illustrates most of the phenomena encountered: the formation of one predominant hydrocarbon product, the isomerization reaction, the formation of a dibromobutane, and the thermal instability of *tert*-butyl bromide.

Several products that might reasonably be expected were present in very minute amounts or not at all: free bromine, methyl bromide and other lower bromides, and various hydrocarbons such as octanes.

DISCUSSION

Two features stand out on inspecting the products of irradiation: (1) The two straight-chain compounds react similarly. The two branched compounds react much like each other, but they differ from the straight-chain compounds. (2) Isobutyl bromide undergoes more extensive isomerization than the other compounds.

Normal butane and isobutylene are by far the predominant volatile products, except for the *tert*-butyl bromide formed in about the same yield by the isomerization of the isobutyl compound. Very little of the bromine corresponding to the hydrocarbons formed can be accounted for amoung the volatile products. A considerable part of it is found in various dibromobutanes, at least one of which has been identified among the products of each isomer. All the dibromo compounds definitely identified were vicinal dibromides with the second bromine on a carbon atom adjacent to the one bonded to the bromine of the original compound. One and in some cases two other products of low volatility were observed in appreciable amounts; they could possibly be dibromobutanes of different configurations. The yields of these compounds were smaller than those of the identified dibromobutanes, however.

The radiolysis of organic compounds is known to involve highly complex processes. Nevertheless, the fact that very small numbers of products predominate in yield over all others in the irradiation of butyl bromides makes it seem reasonable to assume that there are a few reactions that predominate even though there may be many others occurring.

The observed small number of products and the nature of the products found seem most readily explained if it is assumed that the effect of the radiation is almost always to rupture the carbon-bromine bond. This idea is in agreement with earlier work on halogenated hydrocarbons (*2*, *4*, *5*), and it means that a mechanism must exist for transferring energy from other parts of the irradiated molecule to the carbon-bromine bond.

The isomerization of isobutyl bromide into the tertiary compound is probably related to the known relative stability of the tertiary butyl free radical.

The difference, in regard to the formation of unsaturated hydrocarbons, between the straight-chain and branched compounds was quite clear-cut and reproducible under the conditions of these experiments, but the reason for the difference is not apparent from the structure of the starting materials.

SUMMARY

The γ-ray-induced decomposition of the four isomeric butyl bromides has been studied. Normal butane is the major product from the two straight-chain compounds, and isobutylene from the two branched-chain isomers. A considerable portion of the bromine corresponding to the production of these hydrocarbons has been found to occur, under the conditions of the experiments, as various dibromobutanes. Isobutyl bromide isomerizes extensively into the tertiary bromide. Some implications of the experimental findings have been discussed.

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