The Radiation-Induced Isomerization of 1-Bromobutane by a Free Radical Chain Reaction[1,2]

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Abstract: It has been shown that the radiation-induced isomerization of 1-bromobutane to 2-bromobutane is an autocatalytic reaction in which hydrogen bromide functions as a chain transfer agent. The reaction has been studied as a function of dose, dose rate, temperature, and added hydrogen bromide concentration. Free radical scavengers (DPPH and iodine) inhibit the chain reaction. The presence of hydrogen bromide is essential to chain propagation, and experiments with tritiated HBr show that the tritium atom is transferred from TBr to give both 2-bromobutane and 1-bromobutane as radioactive products. A limiting rate of isomerization is reached at [HBr] $> 10^{-3}$ *M*. In the absence of added hydrogen bromide, the concentration of butenes and HBr each attains a stationary value at very low doses (*ca.* 6×10^{-4} *M* at 30°). The butene products include *cis*- and *trans*-2-butene in addition to 1-butene. It is proposed that bromoalkyl radicals undergo rearrangement through a series of reversible steps which involve elimination of a bromine atom, olefin isomerization, and readdition of Br·.

During the course of another investigation,[3] it was noticed that 1-bromobutane is isomerized to 2-bromobutane with a large *G* value by the action of γ radiation at room temperature or above. Our interest in this reaction was stimulated further by the work of Benson and Willard,[4] who have shown that the radiation-induced isomerization of 1-chloropropane is a free radical chain reaction, which is catalyzed by hydrogen chloride and proceeds according to the following steps.

$$Cl\cdot + CH_3CH_2CH_2Cl \longrightarrow CH_3\dot{C}HCH_2Cl + HCl \quad (1)$$

$$CH_3\dot{C}HCH_2Cl \rightleftharpoons CH_3CHClCH_2\cdot \quad (2)$$

$$CH_3CHClCH_2\cdot + HCl \longrightarrow CH_3CHClCH_3 + Cl\cdot \quad (3)$$

A similar mechanism is said to hold for the γ-induced isomerization of 1-chlorobutane.[5]

In contrast to the results obtained for 1-bromobutane, the *G* value for the conversion of 1-bromopropane to 2-bromopropane is not characteristic of a chain reaction.[2,5,6] Also, it has been shown[5] that the hydrogen halides do not catalyze the γ-induced isomerization of the bromoalkanes in precisely the same way that hydrogen chloride catalyzes the isomerization of the chloroalkanes. These observations are difficult to reconcile with completely analogous isomerization mechanisms for the chloroalkanes and bromoalkanes, and some subtle differences must be involved.[7]

Recent work on the free radical addition of hydrogen bromide to 1-olefins has demonstrated that this reaction, which invariably gives the 1-bromoalkane, is accompanied by isomerization of the olefin.[8,9] In the case of 1-hexene, hydrogen bromide catalyzes the isomerization to 2-hexene in the liquid phase, so that the subsequent addition also leads to the formation of 2-bromo- and 3-bromohexanes.[9] The relevance of these findings to the study of the radiation-induced isomerization of 1-bromobutane became apparent, and this paper reports a full account of the work[2] and its considered interpretation.

Experimental Section

Materials. 1-Bromobutane was obtained as a Superior grade from Matheson Coleman and Bell. In some experiments, this material was washed six times with fresh portions of concentrated sulfuric acid, followed by several washings with aqueous sodium bicarbonate and water. After drying over successive portions of magnesium sulfate, the liquid was distilled over anhydrous sodium carbonate. The omission of the sulfuric acid pretreatment did not affect the results. By gas chromatography, the purity of the final distillate was found to be 99.95–99.98 mol % with 2-bromobutane as the principal impurity. 1-Bromopropane (Eastman) was washed with sulfuric acid and then treated in a manner similar to that described for 1-bromobutane. Iodine was obtained as a resublimed reagent grade, and sublimed once again before use. 2,2-Diphenyl-1-picrylhydrazyl, abbreviated as DPPH, and reagent grade methanol were used as received. Hydrogen bromide (Matheson Research Grade) was obtained as a gas in a lecture bottle and was used directly. Other materials for preparative and analytical work were of reagent grade quality. Tritium bromide was prepared as described below.

Preparation of Samples. All samples for γ irradiation were made up in Pyrex tubes (8–24 mm o.d.) on the vacuum line. For 1-bromobutane without additives, it was important to dry the material thoroughly in order to obtain reproducible results. The distilled material was passed through a column of freshly activated silica gel into the vacuum apparatus, and this treatment proved to be adequate throughout most of the early work. However, a few samples prepared from one batch of material were found to contain a second phase of small droplets, and the γ-induced isomerization yield for these experiments was negligible in comparison with the values obtained for dry samples. The remainder of this contaminated material was allowed to stand over two successive portions of magnesium sulfate on the vacuum line, whereupon the subsequent samples prepared from this batch gave isomerization yields which were restored to the former (dry) values. Since added water is known to depress the isomerization yield (see later), the droplets probably consisted of water. After this experience, the additional drying steps over magnesium sulfate were incorporated into the routine procedure of sample preparation, and no further problems were encountered.

Solutions of water, water and methanol, iodine, and DPPH in 1-bromobutane were made up externally in general, and each was pipetted through a side arm into a sample tube already fixed to the vacuum line. One solution of DPPH was prepared by adding the requisite amount of solid to the empty cell and then distilling in a

(1) This research was supported by the U. S. Atomic Energy Commission under Contract No. AT-(40-1)-2968 at the University of Tennessee. This is AEC Document No. ORO-2968-45.

(2) Based on the Ph.D. Thesis of D. H. Martin, University of Tennessee, 1966.

(3) D. H. Martin and F. Williams, *J. Amer. Chem. Soc.*, **85**, 1014 (1963).

(4) H. L. Benson, Jr., and J. E. Willard, *ibid.*, **83**, 4672 (1961); **88**, 5689 (1966).

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(7) F. R. Mayo, *J. Amer. Chem. Soc.*, **84**, 3964 (1962).

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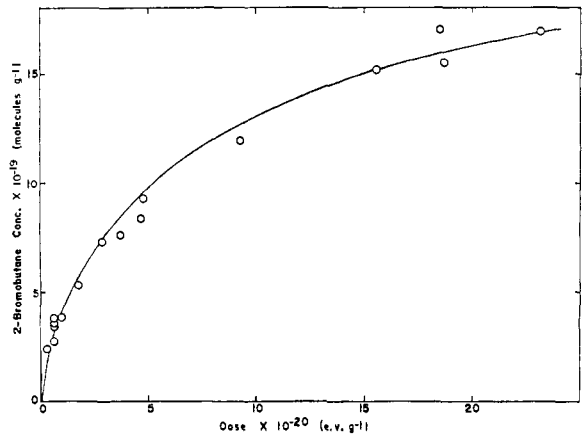

Figure 1. Isomerization of 1-bromobutane at 30° as a function of dose at a dose rate of 3.5×10^{17} eV g^{-1} min^{-1}.

known amount of 1-bromobutane from the reservoir of dry material. The usual operations were followed for complete degassing of liquids.

Hydrogen bromide solutions were prepared on the vacuum line by condensing a known amount of gas (measured by *PVT*) into a sample tube containing 1-bromobutane at 77°K. A mixture of tritium bromide and hydrogen bromide was prepared[2] by the photolytic reaction of excess bromine with hydrogen containing tritium[10] at 350°, and then purified by several trap-to-trap distillations from 195 to 77°K on the vacuum line.

Analytical Methods. A detailed description of the gas chromatographic techniques used in this work is available.[2] The hydrocarbon products, mainly butane and the butenes, were analyzed on a column of either hexanedione or dimethylsulfolane on diatomaceous earth using a thermal conductivity detector, and identified by comparison of their retention times with the values obtained for the Phillips No. 37 hydrocarbon mixture. The analysis for 2-bromobutane was carried out using either a column of Ucon oil (Perkin-Elmer column R) on diatomaceous earth and a thermal conductivity detector, or a column of silicone oil (Perkin-Elmer column C) on Chromosorb and a flame ionization detector. The latter method was used for concentrations of 2-bromobutane down to *ca.* 0.01 mol %, and for the detection of higher boiling products by temperature programming. Quantitative work was carried out by comparison of peak areas with suitable standards. At low concentrations of 2-bromobutane, it was advantageous to use the internal standard technique, whereby known amounts of *t*-butyl bromide were added to the irradiated sample before analysis. The method was calibrated by plotting the relative instrumental response to the known mole ratio of the two compounds in standard samples.

The identification of 2-bromobutane as the main radiolysis product was confirmed by ir and nmr spectroscopy. An aliquot from an irradiated sample was analyzed for 2-bromobutane by gas chromatography, and a matched solution having the same concentration of authentic 2-bromobutane was prepared. Both of these solutions showed ir absorption bands characteristic of 2-bromobutane and the spectra agreed both qualitatively and quantitatively.[2] Since the portion of the irradiated sample which was used for ir examination had not been processed, this experiment proves that 2-bromobutane is formed during radiolysis, and thus eliminates the remote possibility that 2-bromobutane formation might be caused by the breakdown of some other radiolysis product during gas chromatographic analysis. It was also shown[2] that the nmr spectrum of the 2-bromobutane fraction recovered from the irradiated sample by preparative gas chromatography was identical with that of a sample of pure material.

Hydrogen bromide was determined iodometrically[6] by measuring the absorbance of I_3^- at 350 nm. The specific radioactivity of the tritium bromide–hydrogen bromide mixture was determined by liquid scintillation counting, using a solution of the mixture which had been assayed for total hydrogen bromide. A tritiated toluene solution from the New England Nuclear Corp. was available as a standard.

The isotopic dilution technique was used to determine the amount of radioactivity incorporated into 2-bromobutane and 1-bromobutane by the radiolysis of 1-bromobutane in the presence of the ^{3}HBr–HBr mixture. Unreacted HBr was removed by extraction with water and a small portion of the dried sample was analyzed by gas chromatography. The rest of the sample was diluted with nonradioactive 2-bromobutane and the isomers were separated by fractional distillation. Portions of the separated bromobutanes were counted and analyzed; from these results and the dilution factor, the specific activities of the isomers in the irradiated sample were calculated. A negligible amount of radioactivity was incorporated in the bromobutanes by a control experiment in which a sample of unirradiated 1-bromobutane containing 10^{-2} *M* HBr–^{3}HBr was processed in an identical manner.

Dosimetry. Dose rates in 0.8 *N* H_4SO_4 were determined by the standard Fricke method using $G(Fe^{3+}) = 15.6$. The corresponding dose rates in other materials were calculated on the basis of proportionality to the mass absorption coefficients. These coefficients were obtained[2] by evaluating the sum of the individual coefficients for the Compton, photoelectric, and pair production processes for each element and taking the weight-average value for the compound or mixture.

Results

Reaction Products. The main product from the radiolysis of 1-bromobutane at temperatures higher than 30° is 2-bromobutane. An exception to this statement might be made at extremely low doses below 10^{17} eV g^{-1}, where there is an indication of an induction period (see below); but otherwise the isomerization is always the dominating reaction over the entire range of conditions of total dose, dose rate, temperature, and added hydrogen bromide concentrations, which have been investigated in the course of this work. Moreover, the magnitude of the *G* values for 2-bromobutane formation immediately characterize the isomerization as a chain reaction.

Additional products of 1-bromobutane radiolysis include *n*-butane, 1-butene, *cis*- and *trans*-2-butene, hydrogen bromide, and components having higher boiling points than 1-bromobutane. No evidence was obtained for other products having retention times lower than 1-bromobutane. Evidence is presented below that the reactions leading to formation of the olefin products and hydrogen bromide are intimately associated with the detailed mechanism of the isomerization. A quantitative study of the reaction has been carried out as a function of several variables, and the results will now be described in detail.

Effect of Dose on the Isomerization of 1-Bromobutane. The isomerization reaction shows a marked dose dependence at total doses exceeding *ca.* 1×10^{20} eV g^{-1}, and as shown in Figure 1, the concentration of 2-bromobutane does not increase linearly with dose at such high doses. This behavior cannot be attributed to the attainment of high conversions, since the highest concentration in Figure 1 only corresponds to *ca.* 5 mol % 2-bromobutane. It is much more likely that the deviation from linear concentration–dose plots is caused by the buildup of secondary products, which proceed to interfere with the reactions leading to isomerization. This aspect of the work was not explored in detail but the presence of other products was verified in samples that had received large doses. By gas chromatography, 13 products with retention times greater than that of the bromobutane isomers were detected in a sample of 1-bromobutane irradiated at 30° to a total dose of 6.9×10^{19} eV g^{-1}, whereas such products were not de-

(10) The mixture contained *ca.* 5×10^{-6} mole fraction of tritium and had been passed over platinized asbestos to remove oxygen, and through a trap at 77°K to remove traces of water and other condensables. We are indebted to Dr. S. Akhtar for providing us with this material.

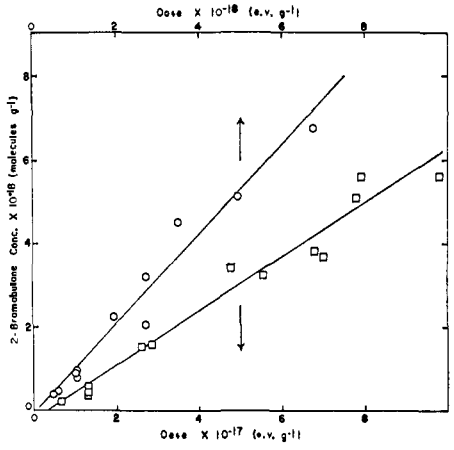

Figure 2. Isomerization of 1-bromobutane at 30° as a function of dose at low doses: O, dose rate 3.3×10^{17} eV g^{-1} min^{-1}; □, dose rate 4.4×10^{15} eV g^{-1} min^{-1}.

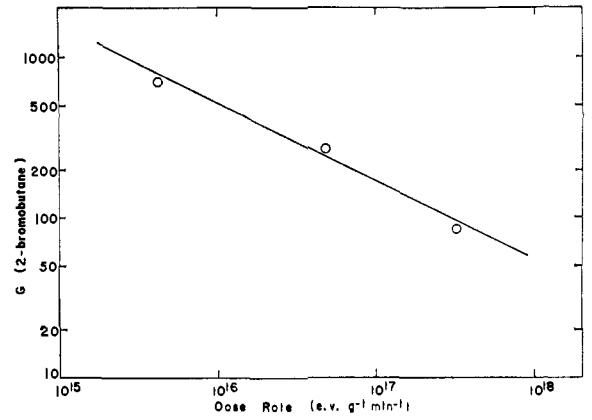

Figure 3. Dependence of the integral G(2-bromobutane) on dose rate at 30°. The total dose in each experiment was 4.8×10^{17} eV g^{-1}.

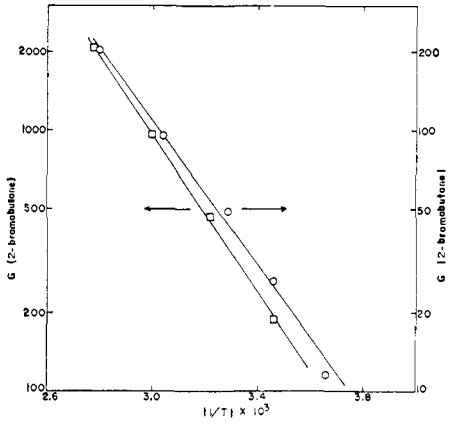

Figure 4. Dependence of G(2-bromobutane) on temperature: O, dose rate 3.8×10^{17} eV g^{-1} min^{-1}, total dose 6.9×10^{19} eV g^{-1}; □, dose rate 4.5×10^{15} eV g^{-1} min^{-1}, total dose 1.3×10^{17} eV g^{-1}.

tectable under exactly the same analytical conditions[2] for a sample that had received a dose of 1.0×10^{18} eV g^{-1}. In the former case the G value for the most abundant of these other products was *ca.* 0.5 as compared to an integral G(2-bromobutane) of 55 under the same irradiation conditions. Thus it is probable that at low doses, the less volatile products of 1-bromobutane radiolysis represent only an insignificant fraction of the total amount of 1-bromobutane converted, and at least from a practical point of view, the isomerization may be considered to be a relatively clean reaction.

Effect of Dose Rate and Temperature on the Isomerization. To avoid complications stemming from other processes, the isomerization has been studied at low total doses. Figure 2 shows that when the dose rate is held constant, the concentration–dose plot is linear below 10^{19} eV g^{-1}. The existence of a small intercept on the dose axis implies that a short induction period may elapse at the start of irradiation before the formation of 2-bromobutane. A dose rate dependence of the G value is revealed by the two plots in Figure 2, the differential G values for isomerization at 30° being 656 and 107 at 4.4×10^{15} and 3.3×10^{17} eV g^{-1} min^{-1}, respectively. Willard and coworkers[5] have reported a G value of 10 for doses up to 1.6×10^{20} eV g^{-1} at 25°, and a dose rate of 3.5×10^{18} eV g^{-1} min^{-1}. This result is consistent with our findings, since the G value is diminished by lowering the temperature (see later) and by increasing the dose rate. In an earlier study, Wilcox[11] obtained a G value of 0.2 at a total dose of 9.5×10^{21} eV g^{-1}, but our work now shows that such a low value is quite unrepresentative of the radiolysis at low doses.

The logarithmic plot in Figure 3 shows the dependence of G (2-bromobutane) on dose rate for three runs carried to the same total dose of 4.8×10^{17} eV g^{-1}. As shown in Figure 2, this dose is well within the linear concentration–dose region, irrespective of the dose rate. It should be noted here that the integral G values so obtained differ slightly from the differential G values mentioned earlier when comparison is made at about the same dose rate. In general, the integral G value will be slightly less than the differential G value because of the small positive dose intercept in the linear concentration–dose plot. Thus the integral G value of 83 plotted in Figure 3 is less than the differential G value of 107 deduced from Figure 2, at a similar dose rate of 3.3×10^{17} eV g^{-1} min^{-1}. Also, we find that the differential G values give a dose rate exponent of −0.42, whereas the integral G values in Figure 3 give a slope of almost exactly −0.50. No particular significance is attached to this numerical difference, and these results suggest that the isomerization reaction is a chain process in which the termination reactions are second order in propagating species.

In Figure 4, the temperature dependence of G(2-bromobutane) is displayed. Two sets of results are shown, corresponding to different conditions of dose rate and total dose. The larger set of G values was obtained at the lower dose rate and at a total dose in the range for which the concentration–dose plot is linear (Figure 2). This latter criterion was not satisfied for the results that refer to the higher dose rate, and therefore these integral G values are much lower than the initial differential value which would apply under the same conditions. However, each set of data obeys an Arrhenius relation for the temperature dependence, corresponding to activation energies of 6.5 and 7.2 kcal/mol at the upper and lower dose rates, respectively, and it is reassuring that such good agreement has been achieved in the circumstances.

Effect of Radical Scavengers on the Isomerization. The presence of 2.5×10^{-3} M iodine in 1-bromobutane

(11) W. S. Wilcox, *Radiat. Res.*, 10, 112 (1959).

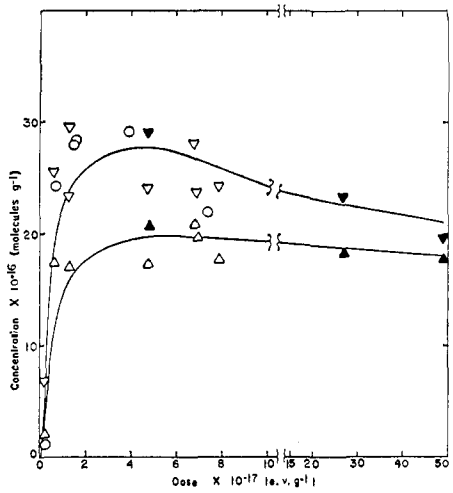

Figure 5. Production of butenes and HBr at 30° as a function of dose: ○, [HBr]; ▽▼, total [butenes]; △▲, [2-butenes]. The open and solid triangles refer to dose rates of 4.3×10^{16} eV g^{-1} min^{-1} and 3.2×10^{17} eV g^{-1} min^{-1}, respectively.

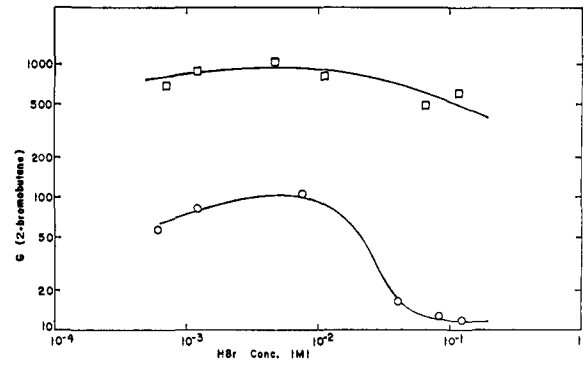

Figure 6. Dependence of G(2-bromobutane) at 30° on [HBr]: □, dose rate 4.3×10^{16} eV g^{-1} min^{-1}, dose 1.3×10^{17} eV g^{-1}; ○, dose rate 3.2×10^{17} eV g^{-1} min^{-1}, dose 6.9×10^{19} eV g^{-1}.

virtually eliminated the radiation-induced isomerization. In two separate runs at 31 and 83°, samples of this solution were each irradiated to a total dose of 6.8×10^{19} eV g^{-1} and gave no detectable amounts of 2-bromobutane ($G < 0.1$). A similar negative result was obtained for a solution containing 1.1×10^{-3} M DPPH after a dose of 8.8×10^{17} eV g^{-1} at 30°. In another run where the initial DPPH concentration was 0.97×10^{-3} M, an irradiation dose of 6.9×10^{19} eV g^{-1} at 30° produced 2-bromobutane with a G value of 0.6. However, the color of DPPH was removed during this irradiation, and a calculation according to Clendinning's value[12] of 3.7 for G(–DPPH) in 1-bromobutane indicates that the scavenger was completely depleted after about a third of the total dose.

Production of Hydrogen Bromide and Butenes. In Figure 5, the concentration of total butenes and of the 2-butenes are shown as a function of dose. It is striking that a "stationary" concentration of these olefinic products was attained at a very low dose ($<2 \times 10^{17}$ eV g^{-1}). The results for hydrogen bromide production are also plotted in Figure 5, and it is evident that here again the concentration increased rapidly at first, only to become more or less constant on continued irradiation. It is interesting that the dose required to attain the "stationary" concentrations of these products is roughly comparable to the induction dose for the formation of 2-bromobutane (Figure 2). The distribution of butene isomers altered as a function of dose. Initially, 1-butene appeared to predominate over the sum of the *cis*- and *trans*-2-butenes; but at the higher doses, the ratio of 1-butene to 2-butenes was 1:3 and approximately constant. The ratio of *cis*- to *trans*-2-butene at 30° agreed to within 10% of the equilibrium value calculated from thermodynamic data.[13]

The "stationary" concentrations of HBr and the butenes increased when the radiolysis was carried out at higher temperature. At 87° these concentrations were both close to 6.0×10^{-3} M, which may be compared to 5.8×10^{-4} M at 30° (Figure 5). From the temperature dependence of the equilibrium constants derived from the above results, we obtain an enthalpy change of −18 kcal referred to a standard state of 1 M for the addition of HBr to the butenes. The enthalpy change for the addition of HBr to ethylene in the gas phase at 25° and 1 atm pressure is calculated to be −19.1 kcal from the appropriate heats of formation.[14] Similar calculations using an estimated value[14] of −24.1 kcal for the heat of formation of bromobutane give enthalpy changes of −15.4, −13.7, and −12.7 kcal for the addition of HBr to 1-butene, *cis*-2-butene, and *trans*-2-butene, respectively. Thus the present experimental result is in reasonable agreement with the information from thermochemistry.

Effect of Added Hydrogen Bromide on the Isomerization. Figure 6 shows that *added* hydrogen bromide does not exert a strong "catalytic" effect on the radiation-induced isomerization of 1-bromobutane. The G values are increased about twofold at *ca.* 10^{-2} M HBr over the corresponding values without added HBr. The addition of 7×10^{-4} M HBr resulted in an *integral* G value of 675 (Figure 6) which corresponds almost exactly to the *differential* G value at this dose rate (Figure 2) in the absence of added HBr. As already mentioned, a "stationary" HBr concentration of *ca.* 6×10^{-4} M (at 30°) is built up in the latter case, so the comparison of results with the differential G value can only reveal the effect of HBr concentrations which exceed this value. There seems to be a decrease in the G value for isomerization at HBr concentrations greater than 10^{-2} M, and this effect is much more pronounced for the experiments at high dose rate and high dose.

Effect of Added Water and Methanol on the Isomerization. It has been mentioned in the Experimental Section that unduly low G values for isomerization were obtained for certain samples which had apparently become "wet" by accident. Further experiments on samples to which water was intentionally added gave results that confirmed the negative effect of water on the isomerization yield. At 31° for a water-saturated sample of 1-bromobutane, the G value for isomerization was only 5.7 compared to 49 (mean of four runs) for a dry sample under the same irradiation conditions (dose rate of 3.8×10^{17} eV g^{-1} min^{-1} and total dose of 6.9×10^{19} eV g^{-1}). In the case of a water-saturated sample

(12) W. R. Clendinning. Ph.D. Thesis, University of Michigan, 1960.
(13) A. Maccoll and R. A. Ross. *J. Amer. Chem. Soc.*, 87, 1169 (1965).
(14) (a) "Selected Values of Chemical Thermodynamic Properties." National Bureau of Standards Circular 500. U. S. Government Printing Office, Washington. D. C., 1950; (b) S. W. Benson. "The Foundations of Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, pp 662–669.

Table I. Tritium Incorporation in Bromobutanes by γ-Radiolysis of Liquid 1-Bromobutane[a] in the Presence of 10^{-2} M Tritiated Hydrogen Bromide[b]

Dose, eV $g^{-1} \times 10^{-17}$	HBr–TBr concn, $M \times 10^2$	G(2-bromobutane), molecules/100 eV	Specific activity of 2-bromobutane dpm/μmol	Specific activity of 1-bromobutane, dpm/μmol	Ratio of total activity in 2-bromobutane to that in 1-bromobutane
0.63	1.08	480	3.6×10^5	23	1.1
1.26	1.14	750	1.3×10^5	37	0.7
1.26	1.06	940	3.5×10^5	72	1.3
2.53	1.05	1100	2.2×10^5	183	0.8

[a] Temperature = 30° and dose rate = 4.2×10^{15} eV g^{-1} min^{-1}. [b] Specific activity = $8.0 \pm 0.6 \times 10^5$ dpm/μmol.

containing 1 mol % added methanol, no isomerization could be detected ($G < 0.1$) after a similar irradiation exposure. At 82°, irradiation of a water-saturated sample as before gave a G value of 206, which is almost the same as that obtained for a dry sample under identical conditions (Figure 4), but the G value was reduced to 50 for a water-saturated sample containing 1 mol % methanol.

Isomerization in the Presence of Tritiated Hydrogen Bromide. To elucidate the role of HBr in the mechanism of isomerization, experiments were carried out to determine the extent of tritium incorporation into both 1-bromobutane and 2-bromobutane by radiolysis of 1-bromobutane in the presence of tritiated HBr. A summary of the results is given in Table I. Very low doses were used in order to obtain information that was strictly relevant to the previous measurements, and the two G values for isomerization at the dose of 1.26×10^{17} eV g^{-1} are comparable to the value of 803 obtained at a dose of 1.31×10^{17} eV g^{-1} in the presence of 1.1×10^{-2} M HBr (nonradioactive) at the same temperature and dose rate (Figure 6). From the fact that 2-bromobutane is formed with a specific activity which is of the same order of magnitude as the tritiated HBr, it is clear that HBr must be involved in the isomerization. The difference between the specific activities of the tritiated HBr and the 2-bromobutane product is probably due in part to a kinetic isotope effect. It is interesting that tritium is also incorporated in 1-bromobutane, and the specific activity increases with the dose as would be expected for a γ-induced exchange reaction. The ratio of total activities induced in the two isomers is near unity, and this result implies that the reactions leading to the formation of 1-bromobutane and 2-bromobutane through the intermediacy of HBr occur with about equal rates.

Production of *n*-Butane. The concentration of *n*-butane was measured in 13 samples of 1-bromobutane which had been irradiated for total doses between 6.8×10^{17} and 2.32×10^{21} eV g^{-1}. Over this range, G(*n*-butane) shows an increasing trend from 2.5 to 3.8 with a mean value of 3.2.

Isomerization of 1-Bromopropane. After a total dose of 6.9×10^{19} eV g^{-1} at 30°, 2-bromopropane was formed with a G value of 2.4. Neddenriep and Willard[6] have reported a G value of 2.1 for irradiation doses between 2 and 9×10^{20} eV g^{-1}.

Discussion

The mechanism of the radiation-induced isomerization of 1-bromobutane will be considered in terms of the elementary reactions 4 through 12. Termination reactions have been omitted from the scheme, but these are taken to include bimolecular processes which proceed randomly between the allylic radicals, Br·, $CH_3CH_2\dot{C}HCH_2Br$, and $CH_3\dot{C}HCHBrCH_3$.

$$CH_3CH_2CH_2CH_2Br \dashrightarrow CH_3CH_2CH_2CH_2\cdot + Br\cdot \quad (4)$$

$$Br\cdot + CH_3CH_2CH_2CH_2Br \rightleftharpoons HBr + CH_3CH_2\dot{C}HCH_2Br \quad (5)$$

$$CH_3CH_2\dot{C}HCH_2Br \rightleftharpoons CH_3CH_2CH{=}CH_2 + Br\cdot \quad (6)$$

$$Br\cdot + CH_3CH_2CH{=}CH_2 \rightleftharpoons HBr + CH_3\dot{C}HCH{=}CH_2 \quad (7)$$

$$CH_3\dot{C}HCH{=}CH_2 \longleftrightarrow CH_3CH{=}CHCH_2\cdot \quad (8)$$

$$CH_3CH{=}CHCH_2\cdot + HBr \rightleftharpoons CH_3CH{=}CHCH_3 + Br\cdot \quad (9)$$

$$CH_3CH{=}CHCH_3 + Br\cdot \rightleftharpoons CH_3\dot{C}HCHBrCH_3 \quad (10)$$

$$CH_3\dot{C}HCHBrCH_3 + HBr \longrightarrow CH_3CH_2CHBrCH_3 + Br\cdot \quad (11)$$

$$CH_3CH_2CH_2CH_2\cdot + HBr \longrightarrow CH_3CH_2CH_2CH_3 + Br\cdot \quad (12)$$

Before analyzing the above scheme in detail, it is useful to summarize the main lines of evidence in support of this general interpretation. (a) The chain character of the isomerization is manifested by the large G values, particularly at low dose rates and elevated temperatures. (b) Although added HBr does not bring about a strong catalytic effect, the results obtained with tritiated HBr definitely show that 2-bromobutane is formed by hydrogen transfer from HBr. Since HBr is itself produced by the radiolysis of 1-bromobutane, the isomerization may be regarded as an autocatalytic process which functions efficiently at extremely low HBr concentrations. Also, the reduction in the isomerization yield by added water or water–methanol is explicable if these polar compounds "dissolve" HBr and thereby reduce the effective concentration in 1-bromobutane. (c) The complete inhibition of the isomerization by iodine or DPPH in concentrations greater than 10^{-3} M argues for a free radical mechanism. (d) Identification of the 2-butenes as the major fraction of the unsaturated olefin products is strong evidence for the involvement of steps 7, 8, and 9. (e) The chain isomerization of 1-bromopropane according to a similar mechanism would be undetectable without tracers.

Although (4) is the only reaction that leads to the net production of radicals in the above scheme, this is not meant to imply that other bond-rupture processes do not occur by radiolysis, nor should it be assumed that the reaction occurs simply by homolytic cleavage of the carbon–bromine bond. The present study can provide little information about the nature of the fundamental processes leading to the production of free radicals. Evidence for the intermediate *n*-butyl radical comes from the formation of *n*-butane with a mean G value of 3.2. The suggested mechanism of steps 4 and 12 is reasonable, but does not exclude the possibility in-

stead of (12) that the *n*-butyl radical abstracts a hydrogen atom from 1-bromobutane. However, it is clear that *n*-butane is not produced by a chain mechanism, and the value of G(*n*-butane) agrees well with a previous determination[11] of 3.4 at a very high dose, where the isomerization is largely suppressed. Also the result is comparable to G(propane) = 3.5 in the radiolysis of 1-bromopropane,[6] which does not give rise to a chain isomerization.

The position of hydrogen atom abstraction indicated in (5) is supported by two independent studies. First, 1,2-dibromobutane has been identified as a radiolysis product[11] with a G value of 1.0, and this can be taken as evidence of a termination reaction between Br· and the bromobutyl radical formed in (5). Similarly in the photobromination of liquid 1-bromobutane,[15] 1,2-dibromobutane constitutes 85% of the dibromide product; again it is likely that hydrogen atom abstraction occurs by (5) in the 2 position, followed in this case[15] by reaction of the bromobutyl radical with either atomic or molecular bromine.

Steps 5 through 11 are indicated to be reversible processes. The bromination of several saturated hydrocarbons has been shown[16] to involve reversible reactions analogous to eq 5, 7, 9, and 11. Moreover, the reverse of (5) and the forward step in (11) are established reactions in the mechanism of free radical addition of HBr to alkenes.[7] Reversibility of bromine atom addition to olefins as implied by eq 6 and 10 is usually regarded as being responsible for the catalysis of *cis–trans* isomerization.[17] Finally, the mechanism of olefin isomerization by double bond migration according to eq 7, 8, and 9 has been clearly revealed in some recent studies.[8,9] Therefore all the component reactions included in the above scheme are well founded on the basis of many previous studies on related systems.

As we remarked in the introduction, a major puzzle was originally presented by the need to account for the radiation-induced isomerization of 1-bromobutane but not of 1-bromopropane by a chain mechanism. This selectivity could hardly be explained if the mechanism were to involve a simple intramolecular 1,2 shift of the bromine atom in the bromoalkyl radical. Although Skell and coworkers[18] have obtained evidence for the reverse rearrangement in the bromoalkyl radical produced by the removal of a hydrogen atom from the methyl group of 2-bromopropane, they found no indication that 1,2 migration of a bromine atom had occurred after hydrogen atom abstraction from the 2 position in 1-bromopropane. Another argument against the 1,2 shift mechanism is Gale's recent finding[9] that 2-bromohexane is produced only after 1-hexene has been isomerized to the 2-hexenes during the process of HBr addition. Therefore it must be concluded that either the rate constant for the 1,2 shift is too low, or else the equilibrium is highly unfavorable to the less stable radical which is produced by the shift, and consequently this distribution is reflected in the products of reaction with HBr since low activation energies are involved.[7]

Because the isomerization of 1-bromobutane is represented as the net result of several reversible steps, it is difficult to give a simple kinetic treatment for the reaction. Both the isomerization and the *initial* formation of HBr and butenes occur by a chain process, so the rate of the forward reaction in eq 5 must compete favorably with bimolecular radical termination. The temperature dependence of G(2-bromobutane) from Figure 4 gives an overall activation energy of *ca.* 7 kcal mol^{-1} which probably corresponds to the value for $E_5 - {}^1/_2E_t$. Since the activation energy E_t for diffusion-controlled termination is unlikely to exceed 3 kcal mol^{-1}, E_5 would be *ca.* 8.5 kcal mol^{-1}, which is comparable to the activation energy of 10 kcal mol^{-1} for the attack of a bromine atom on the methylene group of a saturated hydrocarbon.[16]

The principal conclusion that emerges from this work is that the reversible reactions responsible for the interconversion of the bromobutanes must proceed in a balanced manner with relatively low activation energies. In this sequence, the ubiquitous role of the bromine atom is especially noteworthy, and the remarkably facile nature of the overall process must be largely determined by a very close matching of the bromoalkyl-H, butenyl-H, and HBr bond energies. A similar situation does not prevail with the other halogens so that autocatalysis by HBr as revealed by this isomerization reaction is likely to be much more important than in cases where HCl is involved.[4] For example, the rate constant for hydrogen atom abstraction from HBr as in (11) is generally much greater than for the corresponding reaction with HCl.

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