[Contribution from the George Herbert Jones Laboratory of the University of Chicago]

VAPOR PHASE BROMINATION OF ALKYL HALIDES

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The vapor phase bromination[1] of a number of simple alkyl halides was carried out in a specially designed apparatus (Fig. 1). With the low-boiling alkyl halides, the bromination was carried out at atmospheric pressure, and a twenty- to thirty-fold excess of the alkyl halide was always present in the reaction chamber. The reactions, with the alkyl halides of higher boiling point (above 90°), were carried out at reduced pressure, and under these conditions the ratio of alkyl halide to bromine was somewhat smaller.

It is most unfortunate that the experimental difficulties involved in the separation of the reaction products became so great that it was felt prudent not to investigate the products formed by bromination of the alkyl halides beyond the butyl halides. The results cited in Table I were duplicated within close enough limits to assure authenticity.

The reaction products were carefully distilled in a specially designed glass fractionating column[2], efficient enough to separate isomers boiling three or four degrees apart.[3]

ISOMERIZATION

In order to establish the significance of the relative abundance of isomers isolated from the bromination of the alkyl halides, it was necessary to determine whether the products isolated in this study were formed directly or by isomerization, or if the minute traces of iron present in the bromine were responsible for the observed results. It has been previously established in this laboratory (1) that in the presence of traces of iron the liquid and vapor phase bromination of isopropyl bromide gives the 1,2-dibromopropane, whereas the 2,2-dibromopropane is formed exclusively in the absence of small amounts of iron. Similarly, in the presence of small amounts of iron, ethyl bromide gives exclusively the 1,2-dibromoethane, whereas the 1,1-dibromide is formed in the absence of iron. It is reasonable to assume that the reagents used in this study were reasonably free of iron since ethyl bromide and isopropyl bromide gave exclusively 1,1-dibromoethane and 2,2-dibromopropane, respectively.

Isomerization might also occur under the combined influence of light and hydrogen bromide. However, since no change in the refractive index was noted when mixtures of isomers were illuminated (in the presence of hydrogen bromide

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[1] The authors are fully aware that the reactions here described (like many other so-called vapor phase reactions) are not really vapor phase reactions in the "true" sense of that term. They may be "wall reactions", and there may be fine droplets (mist) in the reaction chamber, in spite of the fact that this chamber was heated to a temperature considerably above the boiling point of either reactant.

[2] The Podbielniak columns commercially available were considered unsatisfactory because of the danger of isomerization of the reaction products.

[3] We are indebted to Dr. John Hinckley for much help in the design and construction of this column, as well as the bromination apparatus.

TABLE I

PRODUCTS OF HALOGENATION OF ALKYL HALIDES[a]

Reagents		Pressure in Mm. Mercury	Products	Yield, %
$CH_3CH_2CH_2CH_2Br$	Br_2	200	$CH_3CH_2CHBrCH_2Br$ $CH_3CHBrCH_2CH_2Br$ $C_4H_7Br_3$ $CH_2BrCHBrCHBrCH_2Br$	30 13 30 10 — 83
$CH_3CH_2CHBrCH_3$	Br_2	250	$CH_3CH_2CBr_2CH_3$ $CH_3CHBrCHBrCH_3$ (Meso) $CH_3CHBrCHBrCH_3$ (Racemic) $C_4H_7Br_3$ $CH_2BrCHBrCHBrCH_2Br$	19 22 10 34 6 — 91
$CH_3CH_2CH_2CH_2Cl$	Br_2	500	$CH_3CH_2CH_2CHClBr$ $CH_3CH_2CHBrCH_2Cl$ $CH_3CHBrCH_2CH_2Cl$	23 23 46 — 92
$CH_3CH_2CHClCH_3$	Br_2	Atmospheric	$CH_3CH_2CClBrCH_3$	80
$CH_3CH_2CH_2Br$	Br_2	530	$CH_3CHBrCH_2Br$ $CH_2BrCHBrCH_2Br$	71 18 — 89
$CH_3CHBrCH_3$	Br_2	Atmospheric	$CH_3CBr_2CH_3$	85
$CH_3CH_2CH_2Cl$	Br_2	Atmospheric	$CH_3CH_2CHClBr$ $CH_3CHBrCH_2Cl$	45 45 — 90
CH_3CH_2Br	Br_2[b]	Atmospheric	CH_3CHBr_2	86

[a] Temperature of reaction was 100° unless otherwise indicated. Yields are reported in percent of total bromine consumed by the products.

[b] Reaction temperature: 198°.

at 100°), we may assume that no isomerization of the reaction products took place.

RESULTS

The results obtained in the vapor phase photochemical bromination of a number of alkyl halides are given in Table I. The chlorination experiments given in

TABLE II

PRODUCTS OF HALOGENATION OF ALKYL HALIDES[a]

Reagents		Pressure in Mm. Mercury	Products	Yield (%)
$CH_3CH_2CH_2Cl$	Cl_2	Atmospheric	$CH_3CH_2CHCl_2$	10
			$CH_3CHClCH_2Cl$	27
			$CH_2ClCH_2CH_2Cl$	14
			$C_3H_5Cl_7$	22
				—
				73
$CH_3CH_2CH_2Cl$	Cl_2[b]	Atmospheric	$CH_3CH_2CHCl_2$	5
			$CH_3CHClCH_2Cl$	30
			$CH_2ClCH_2CH_2Cl$	15
				—
				50

[a] Temperature of reaction was 100° unless otherwise indicated. Yields are reported in percent of total chlorine consumed by the products.

[b] Reaction temperature: −78°.

Table II were carried out in a different apparatus (see Fig. 2, experimental part). The experimental part should be consulted for details of the individual experiments.

DISCUSSION

The work here described was undertaken for the following reasons. First, despite the fact that bromination of organic molecules is one of the oldest reactions studied by organic chemists, it must be admitted that the mechanisms which account for the multiplicity of the reaction products are imperfectly understood. Many of the kinetic studies, while interesting, are of little help, since in most of the investigations no products were isolated, and the measurements concerned themselves mainly with the rate of bromine disappearance. Because bromine can disappear from the reaction mixture by more than the simple chain reaction usually postulated for bromination, the measurements from rates of disappearance of bromine do not carry the usual validity. Second, many bromination reactions have been carried out in solution without due regard for the concentration of the bromine, presence of oxygen, traces of metals, illumination, temperature control, presence of inhibitors, etc. All of these factors play an important part not only on the rate of the disappearance of the bromine but also in determining the composition of the reaction mixture.

No claim for a final solution of this problem is made. Rather, this report is intended to indicate the inherent difficulties of this problem and to outline some tentative hypotheses which seem to us attractive.

Brominations in solution, as they have been carried out in the past, have been imperfectly described and usually have had a preparative objective in mind. Because of the large effects of the various factors mentioned above, it is difficult to reconcile the results of many of these studies beyond the statement that the reaction in question is a free radical chain reaction involving bromine atoms.[4] It might be expected that the vapor phase bromination of alkyl halides, where the bromine is introduced very slowly and in the presence of a very large excess of the alkyl halide, would more nearly correspond to the conditions required by the chain reaction given below, if the necessary activation energy is supplied for step 2.

1. $$Br_2 \xrightarrow{h\nu} 2Br\cdot$$

2. $$RH + Br\cdot \rightarrow R\cdot + HBr$$

3. $$R\cdot + Br_2 \rightarrow RBr + Br\cdot$$

This simple formulation may well account for the formation of ethylidene bromide (86%) in the bromination of ethyl bromide.[5] The results could be reconciled on the basis that it requires a lower activation to attack the hydrogen atom of the $—CH_2Br$ group than a hydrogen atom of the methyl group. There is

4. $$CH_3CH_2Br + Br\cdot \rightarrow CH_3\underset{\bullet}{C}HBr + HBr$$

5. $$CH_3\underset{\bullet}{C}HBr + Br_2 \rightarrow CH_3CHBr_2 + Br\cdot$$

another implicit assumption in equation 5, namely that the free $CH_3\underset{\bullet}{C}HBr$ is not readily attacked by a bromine atom to give vinyl bromide and hydrogen bromide.

6. $$CH_3\underset{\bullet}{C}HBr + Br\cdot \rightarrow CH_2{=}CHBr + HBr$$

From the foregoing, it should be obvious that although it is of prime importance which hydrogen atom is first attacked by a bromine atom, it is of equal (or even of greater) importance to know (insofar as the final reaction products are concerned) whether the free radical reacts more readily with bromine molecules or bromine atoms, and the relative concentration of these reagents. Obviously, for complete elucidation of the mechanism it is necessary to know the rates at which different secondary hydrogen atoms are attacked by bromine atoms,[6] the relative stability of the free radicals formed, and whether the free radicals are of a type that can attack a bromine molecule, or whether they disproportionate by themselves or with a bromine atom (leading to an olefin and hydrogen bromide). Thus, the bromination of *n*-propyl bromide to give 45 per

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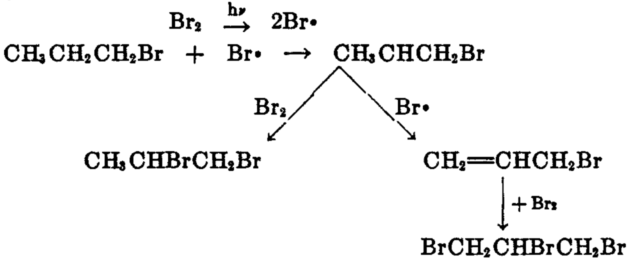
[4] For evaluation of many factors which influence bromination (accelerators as well as retarders) see Kharasch, Hered, and Mayo, *J. Org. Chem.*, **6**, 817 (1941); Kharasch and Hobbs, *J. Org. Chem.*, **6**, 705 (1941); Kharasch, White and Mayo, *J. Org. Chem.*, **3**, 33 (1938); *J. Org. Chem.*, **2**, 574 (1938).

[5] Vinyl bromide, if formed, has escaped detection. It is possible that the higher boiling bromides, found in the reaction, resulted from addition of bromine to the vinyl bromide.

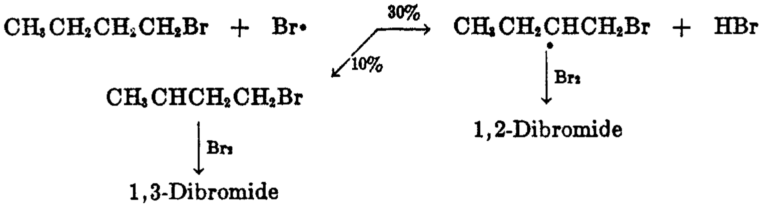
[6] It is our belief that primary hydrogen atoms in alkyl halides are attacked to a negligible extent by bromine atoms at ordinary temperatures.

cent 1,2-dibromopropane and 45 per cent 1,2,3-tribromopropane may be represented schematically as follows:

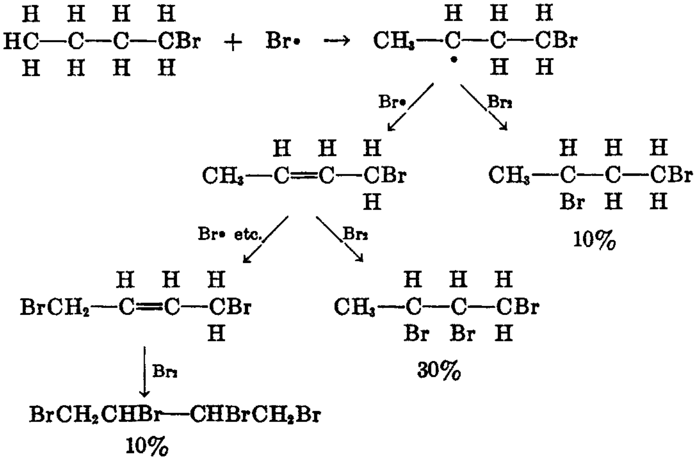


The above formulation (as well as other schemes for the bromination of the other alkyl halides here given) has no great utility, since for predictive purposes the chemistry of the initially formed free radicals must be derived from sources other than the bromination data. In other words, the data on the bromination here recorded indicate that more than one mechanism is responsible for the products of bromination, but do not allow (because of the large number of factors that must be taken into account) the formulation of an hypothesis which will predict accurately the composition of the mixture.

There is an additional uncertainty in the schemes usually written to account for the abundance of the individual isomers. Thus, the customary explanation to account for the formation of the 30 per cent of the 1,2-dibromobutane and 10 per cent of the 1,3-dibromide would be as follows:



However, this formulation ignores entirely the formation of the polybromides. If these are taken into account, a different ratio of the reactivity of the hydrogen atoms (as indicated in the scheme below) suggests itself.



Of considerable theoretical interest are she observations that whereas the bromination of the *n*-propyl, *n*-butyl, and *sec*-butyl chlorides give high yields of the corresponding chloro bromo compounds, and little polyhalogenated compounds, the corresponding bromo compounds give high yields of the polybromides. The interpretation of these results is probably associated with the differences in the stability of free radicals formed by abstraction of a hydrogen atom from an alkyl chloride and an alkyl bromide, respectively.[7]

EXPERIMENTAL PART

Apparatus and procedure. A special apparatus was designed for the vapor phase experiments (see Figure 1). The substance to be brominated was introduced into flask **A** which was heated with a Glass-Col mantle. The substance was distilled through the fractionating column B which was filled with single-turn glass helices. The stopcock **D** was adjusted so that about 50 per cent of the distillate was returned through the fractionating column in order to obtain as much fractionation efficiency as possible. The bromine was introduced from the dropping funnel, **E** and was mixed with the distilled reagent at **F**, and the mixture was passed through a coil into the reaction chamber **H**. The reaction chamber was surrounded by a jacket **L** which was kept at the boiling point of the liquid in flask **K**. In most cases this was water, so that the jacket was kept at 100°, but in the case of ethyl bromide, it was ethylene glycol (198°).

The pressure of the system was adjusted so that all the liquid vaporized while still in the coil. As the vapors flowed through the chamber **H**, they were illuminated by a series of nine 64-candle-power automobile headlight lamps, which were placed in compartment **I** in the center of the reaction chamber in such a manner that the light was distributed through the length of the apparatus. The entire apparatus was surrounded by an aluminum foil reflector.

After leaving the chamber, the vapors were condensed in the condenser **C**, and the condensate was returned to flask **A** through the U-tube **U**, while the hydrogen bromide passed through the condenser **C** and was drawn toward the aspirator. To insure against loss of condensable materials a trap **M**, immersed in a Dry Ice-bath, was inserted into the system.

To keep the lamps from burning out, and also to prevent the inside wall of the reaction chamber from getting too hot, a stream of compressed air was blown through the compartment I during the entire period of the reaction. The bromine was introduced at a rate sufficiently slow so that only a faint trace of color appeared in the condensate returning to the distillation flask through the U-tube. With this arrangement, the reaction proceeded smoothly, and usually the only attention it needed was the adjustment of the rate of flow of the bromine.

It was noted that for the first few minutes of the reaction, the rate was extremely slow. This might have been due to the presence of oxygen in the reaction chamber, although it was generally flushed with nitrogen.

In experiments performed at reduced pressure, the rate of boiling in flask **A** (Figure 1) had to be decreased, since the internal pressure that could be supported by the seal in the U-tube became much less due to the lower pressure above it.

For the liquid phase chlorination of propyl chloride, the apparatus shown in Figure 2 was used. The apparatus consisted of a cylindrical flask into which was sunk a well **A**, which contained three automobile headlight bulbs. Two openings were made in the flask, through one of which extended a stirrer attached to a high-speed motor and through the other a glass tube **B** which reached to the bottom of the flask, next to the blade of the stirrer. Through this tube the chlorine was introduced directly from a small tank of commercial chlorine. The entire apparatus was immersed in a clear Dewar flask which was filled with a Dry Ice-methanol mixture.

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[7] Compare the products formed by the addition of bromotrichloromethane to allyl chloride and allyl bromide, Kharasch, Reinmuth, and Urry, *J. Am. Chem. Soc.*, **69**, 1105 (1947); Kharasch and Sage, *J. Org. Chem.*, **14**, 79 (1949).

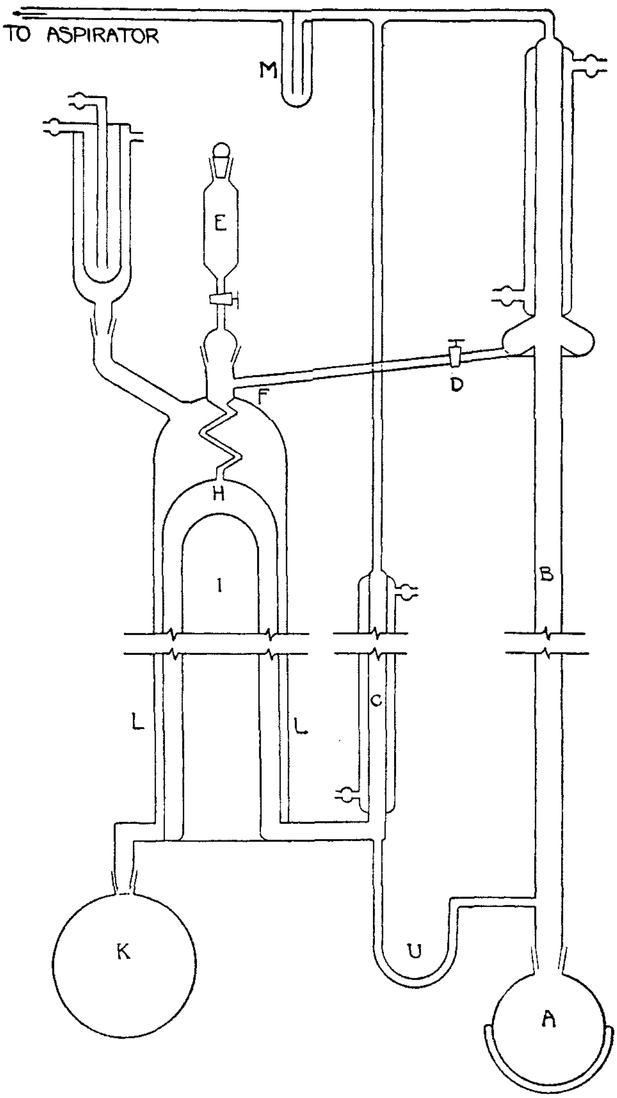

FIG. 1. APPARATUS FOR VAPOR-PHASE BROMINATION.

The separation of the reaction mixtures, after the unchanged alkyl halides had been removed, was carried out in a high-efficiency still. The column consisted of a thermally-insulated 10-mm. tube about 140 cm. long, filled with single-turn glass helices. The condensate was returned to the still through a U-tube to which was attached a stopcock in such a manner that there was absolutely no dead space between it and the tube. The capacity of the U-tube was about 2.5 ml. With the aid of a good pressure-control system, there was no difficulty in maintaining the boiling point of a substance in a range of ±0.02°. Fractions boiling only 3° or 4° apart could be separated quite well, if sufficient time was allowed (between cuts) for the system to reach thermal equilibrium. In order to minimize decomposition, the bottom of the still pot was flat and just barely dipped into the oil of the heating bath. The entire pot was surrounded by a Dewar flask. Since it took several hours for the column to reach equilibrium, a distillation once started was carried through to completion.

Reagents. Commercially available alkyl halides were used in all reactions. The alkyl

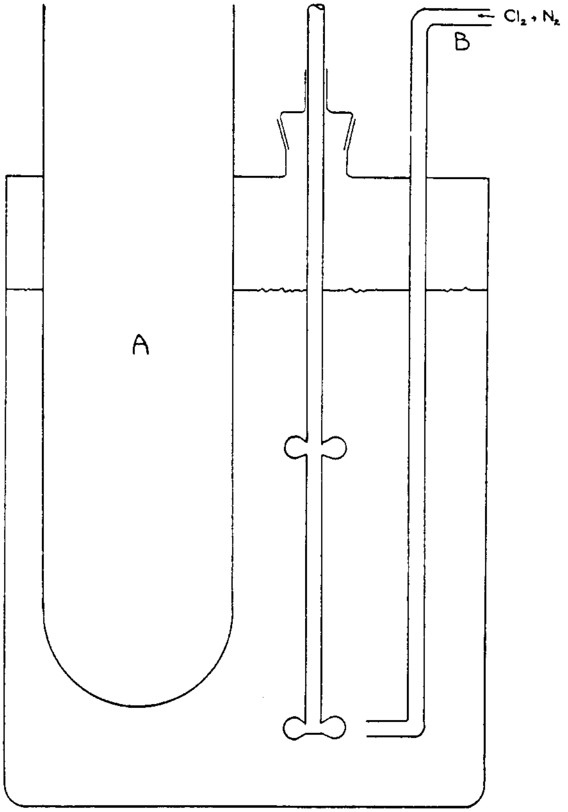

FIG. 2. APPARATUS FOR LIQUID-PHASE CHLORINATION.

halides were purified by stirring with successive quantities of concentrated sulfuric acid in an ice-bath until no change in the color of the acid took place. The acid then was removed and the reagent was washed with sodium bicarbonate solution until neutral. After a final wash with distilled water, the reagent was dried over calcium sulfate and distilled through a Vigreux column; then it was fractionated through a 60-plate column packed with glass-helices. The fractions were kept in individual bottles that had been carefully cleaned and wrapped with aluminum foil. The physical constants of the purified reagents are indicated in Table III.

Distilled bromine (Mallinckrodt N.F.V.) was used in all experiments. The impurities in the bromine were essentially those indicated in the specifications for analytical reagent-grade bromine.

Bromination of ethyl bromide. Ethyl bromide (575 g.) was brominated at 198°. It took ten hours for the introduction of the bromine (180 g.). The unreacted ethyl bromide was removed through a 70-cm. Vigreux column. A high-boiling material (180 g.) remained in the flask.

Distillation of the reaction product through the column (previously described) gave 158 g. (86%) of 1,1-dibromoethane[8] (b.p. 49.32–49.38°/100 mm., n_D^{20} 1.5132; recorded[9] 108–110°, n_D^{20} 1.5128), and 10 g. of residue.

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[8] Throughout this work, yields are reported in per cent of the bromine recovered in the reaction products. For details of the individual distillations, the Doctoral Dissertation of Zimmt (University of Chicago, March 1951) should be consulted.

[9] Where no reference is given, literature values for physical constants are those taken from Beilstein's "Handbuch der Organischen Chemie" or Huntress' "Chlorine Compounds."

TABLE III

PHYSICAL CONSTANTS OF THE ALKYL HALIDES USED IN THIS STUDY[a]

Alkyl Halide	Values Found		Literature Values[b]	
	B.p. (°C.)	n_D^{20}	B.p. (°C.)	n_D^{20}
Ethyl bromide	37.0	1.4223	38.4	1.4244
n-Propyl bromide	69.5–70.0	1.4333	71.0	1.4341
Isopropyl bromide	59.6–59.7	1.4251	59.4	1.4251
n-Propyl chloride	46.7	1.3884	46.6	1.3884
n-Butyl bromide	101.0–101.2	1.4395	101.6	1.4397
sec-Butyl bromide	91.4	1.4367	91.2	1.4370[c]
n-Butyl chloride	78.7	1.4025	78.1	1.4017
sec-Butyl bromide	68.6	1.3960	68.3	1.3970

[a] See text for method of purification.

[b] Where no reference is given, the values were obtained from standard compilations, such as Beilstein's "Handbuch der Organischen Chemie" or Huntress' "Chlorine Compounds."

[c] Timmerman and Delcourt, J. Chim. Phys., **31**, 85 (1934).

That the reaction product was substantially free of 1,2-dibromoethane was shown by heating a 0.6-g. portion of it with 0.4 g. of zinc metal in 15 ml. of 70% aqueous ethanol. The effluent gas was led through a condenser to a trap immersed in a bath at −140°. After one hour the trap was connected to a gas burette and allowed to warm to room temperature. The gas (14 ml.) was shaken with a 2 per cent solution of potassium permanganate. No change in the volume had taken place after 25 minute of shaking. For comparison, a weighed sample of known 1,2-dibromoethane was treated in similar manner. A practically quantitative evolution of gas took place. The gas rapidly decolorized a solution of potassium permanganate.

Bromination of n-propyl bromide. *n*-Propyl bromide (623 g.) was brominated at 100° (520 mm. pressure). It took 11 hours for the introduction of the bromine (220 g.). Upon removal of the unchanged propyl bromide a high-boiling material remained which, upon fractionation, gave 1,2-dibromopropane (200 g.) (b.p. 61.4–61.6°/50 mm., n_D^{20} 1.5195; recorded, b.p. 61.8°, n_D^{20} 1.5200); 1,2,3-tribromopropane (36 g.) (b.p. 92–93°/10 mm., f.p. 16.27°, n_D^{20} 1.5860; recorded f.p. 16°, n_D^{18} 1.584); and about 10 g. of unidentified materials. Treatment of the dibromo fraction with zinc in ethanol gave a gas which condensed at −78°. When the gas was treated with a solution of potassium permanganate, a contraction in volume (85%) was noted (an authentic sample of 1,2-dibromopropane (when similarly treated) gave a contraction in volume of 82%). An 11-g. portion of the 1,2-dibromopropane (reaction product) was converted to the glycol. The bis-phenylcarbamate of the glycol melted at 142.5–144°, and the melting point (2) of this material was not depressed by admixture with an authentic sample.

Bromination of isopropyl bromide. Isopropyl bromide (776 g.) was brominated at 100°. It took ten hours for the introduction of the bromine (232 g.). Upon removal of most of the unreacted isopropyl bromide, a high-boiling material was obtained (292 g.). Upon distillation the following fractions were obtained: Fraction *1*, 2,2-dibromopropane (249 g.; b.p. 46.0–46.2°/70 mm.; n_D^{20} 1.4983; recorded (3) n_D^{20} 1.4977); Fraction *2*, Residue (4 g.). One gram of the presumed 2,2-dibromopropane was refluxed with the 2,4-dinitrophenylhydrazine reagent. The precipitate which formed melted at 125°, and the melting point was not depressed by admixture with an authentic sample of the 2,4-dinitrophenylhydrazone of acetone.

Bromination of n-propyl chloride. *n*-Propyl chloride (509 g.) was brominated at 100°. It took nine hours for the addition of the bromine (240 g.). At the end of the reaction, the unreacted *n*-propyl chloride was removed leaving behind a high-boiling liquid (230 g.). Upon distillation of this material the following fractions were obtained: Fraction *1*, 1-chloro-1-bromopropane (105 g.; 45 per cent; b.p. 45.96–46.01°/75 mm., n_D^{20} 1.4691; recorded, b.p. 47.8°/75 mm., n_D^{20} 1.4703); Fraction *2*, 1-chloro-2-bromopropane (107 g.; b.p. 50.52–50.56°/75 mm., n_D^{20} 1.4788; recorded, b.p. 52°/75 mm., n_D^{20} 1.4795). A residue (14 g.) remained in the distillation flask. This residue was not investigated further since it boiled over a large temperature range and did not appear to contain any one material in appreciable quantity.

The dimethone derivative of propionaldehyde (m.p. 153–153.5°, recorded m.p. 154–156°) was obtained following hydrolysis of the 1-chloro-1-bromopropane with water and sodium bicarbonate at 95–100°. Furthermore, treatment of the 1-chloro-2-bromopropane with zinc and 70 per cent ethanol gave a condensible gas (propylene) which was unsaturated (80%).

Bromination of n-butyl bromide. n-Butyl bromide (1200 g.) was brominated at 100° and a pressure of 200 mm. It took 17 hours for the introduction of the bromine (495 g.). After removal of the unreacted butyl bromide, a residue (520 g.) was obtained. The reaction mixture was distilled at reduced pressure (15 mm./Hg) and the volatile material was collected. About 15 g. of a solid (1,2,3,4-tetrabromobutane) remained in the distilling flask. This material upon crystallization from carbon tetrachloride melted at 116°.

The volatile material was distilled through a fractionating column and the following fractions were collected: Fraction *1*, 1,2-dibromobutane (135 g.; b.p. 60.2°/20 mm.; n_D^{20} 1.5146; recorded, b.p. 50.8°/13 mm.; n_D^{18} 1.5161); Fraction *2*, mostly 1,3-dibromobutane (13%) contaminated with some unsaturated halide; Residue (30%). This product was mostly a tribromobutane (*Anal.* Calc'd for $C_4H_7Br_3$: Br, 81.3. Found: Br, 81.8).

The unsaturated halide was removed from Fraction *2* by conventional means, and the resulting material was distilled through a Vigreux column. The following fractions were collected: Fraction *2a*, b.p. 69–71°/20 mm.; n_D^{20} 1.5091; Fraction *2b*, b.p. 71°/20 mm.; n_D^{20} 1.5090. No reliable physical constants are recorded for 1,3-dibromobutane. Purification of a commercial sample of 1,3-dibromobutane gave a material which boiled at 68.8°/20 mm., and which had an index of refraction (20°) of 1.5090.

Some of the 1,2-dibromobutane (obtained in this study) was treated with zinc and 70% ethanol, and the gas evolved was condensed. About 64% of the gas was unsaturated. Similar treatment of known 1,2-dibromobutane gave 65% of an unsaturated condensible gas.

The melting point of the bis-(S-alkyl)isothiourea picrate prepared from the 1,2-dibromobutane obtained in this study was 209–211°. The melting point was not depressed upon admixture with the bis-(S-alkyl)isothiourea picrate prepared from an authentic sample of 1,2-dibromobutane. The bis-(S-alkyl)isothiourea picrates prepared from known 1,3-dibromobutane, and the 1,3-dibromobutane of Fraction *2a* and Fraction *2b* melted at 221–222°, respectively. No depression in melting point was noted upon admixture of these materials.

Bromination of sec-butyl bromide. sec-Butyl bromide (571 g.) was brominated at 100° (250 mm. pressure). The bromine (270 g.) was added over a period of five hours. After removing the unreacted *sec*-butyl bromide a residue (305 g.) remained. Distillation of the residue through a fractionating column indicated the presence of three dibromo compounds. Two of these were obtained in pure state. The lower-boiling fraction (19%) is assumed to be the 2,2-dibromobutane (b.p. 63.2–63.4°/50 mm., n_D^{20} 1.5007). No physical constants for this substance are recorded in the literature. The second fraction is assumed to be *meso*-2,3-dibromobutane (b.p. 72.7–73.0°/50 mm., n_D^{20} 1.5108; d_{20}^{20} 1.7820; Recorded, b.p. 72.7–72.9°/50 mm., n_D^{20} 1.5116; d_{20}^{20} 1.7827). All of the fractions of the third substance were not of equal purity. However, the higher-boiling fractions were assumed (from the index of refraction) to be fairly pure racemic 2,3-dibromobutane. This assumption was confirmed by a density determination (d_{20}^{20} 1.7915). The recorded density for racemic 2,3-dibromobutane is d_{20}^{20} 1.7916.

Fraction *3* is probably a mixture of tribromobutanes. Seven fractions of 2 ml. each boiled at 62.6–64.6°/5 mm. and had a range of refractive indices of n_D^{20} 1.5685–1.5698. This fraction must be very rich in 1,2,3-tribromobutane which is recorded to have an index of refraction of 1.5691.

From the residue, several grams of the high-melting (116°) 1,2,3,4-tetrabromobutane were isolated.

Bromination of n-butyl chloride. n-Butyl chloride (571 g.) was brominated at 100°. The pressure in the apparatus was maintained at 500 mm. It took seven hours for the introduction of the bromine (315 g.). After removal of the unreacted butyl chloride, the residue (335 g.) was distilled. Three fractions, presumably 1-chloro-1-bromobutane, 1-chloro-2-bromobutane, and 1-chloro-3-bromobutane were collected. Of the three compounds, only the 1-chloro-2-bromobutane has been reported in the literature. The identity of the other two compounds was inferred from the similarity of the physical constants with those of the corresponding dibromo compounds. Thus, the boiling point of 1,3-dibromobutane is higher and the refractive index lower than that of the corresponding 1,2 compound. The 1,1-dibromobutane has a lower boiling point than the 1,2-dibromobutane. The boiling point and refractive index of 1-chloro-1-bromopropane are lower than those of the 1-chloro-2-bromopropane. The compounds isolated had the following physical constants (Table IV).

The physical constants given in the literature for 1-chloro-2-bromobutane are: b.p. 146–147°/755 mm., n_D^{20} 1.4800.

Anal. Calc'd for C_4H_8BrCl: Mol. wt. 171.5; g. AgX/g. sample, 1.931. Found (1-Cl-1-Br): Mol. wt. 170; g. AgX/g. sample, 1.920. Found (1-Cl-3-Br): Mol. wt. 170; g. AgX/g. sample, 1.935.

The presumed 1-chloro-1-bromobutane was hydrolyzed by heating (150°) in a sealed tube with lead oxide. The water layer was treated with a water solution of dimethone. The solid which separated melted at 140–142°, and was not depressed by admixture with an authentic sample of the dimethone of butyraldehyde (m.p. 141°). The 1-chloro-2-bromobutane, when heated with zinc and ethanol, gave a condensible gas which was unsaturated (65%). The 1-chloro-3-bromobutane was treated with thiourea and picric acid to give 1,3-bis-(S-alkyl)-isothiourea picrate (m.p. 217–218°). The melting point was not depressed when admixed with the similar derivative of known 1,3-dibromobutane (216–219°). The 1-chloro-3-bromobutane, when heated with zinc in ethanol, gave a condensable gas which contained 16% unsaturation. This figure is in excellent agreement with the amount of unsaturation (15%) found when known 1,3-dibromobutane is heated with zinc and ethanol.

Bromination of sec-butyl chloride. sec-Butyl chloride (398 g.) was brominated at 100°. It took 4.5 hours for the introduction of the bromine (240 g.). After removal of the unreacted halide a residue (230 g.) was obtained. The residue was distilled. There was only one large fraction (80%) which boiled at 45.2–45.3°/50 mm. (n_D^{20} 1.4653). This material was identified as 2-chloro-2-bromobutane by hydrolysis to methyl propyl ketone. The 2,4-dinitrophenylhydrazone of this ketone melted at 114–116°, and was not depressed by admixture with an authentic sample which melted at 117°.

Anal. Calc'd for C_4H_8BrCl: Mol. wt. 171.5; g. AgX/g. sample, 1.931.

Found: Mol. wt. 173; g. AgX/g. sample, 1.936.

A small amount of a substance (b.p. 54–55°/50 mm., n_D^{20} 1.4785) was found upon distillation of the residue. This may be 2-chloro-3-bromobutane. About 10 g. of higher-boiling product was also formed.

Chlorination of n-propyl chloride. n-Propyl chloride (700 g.) was chlorinated at 100° in the apparatus given in Figure 1. The unreacted propyl chloride was removed and the residue

TABLE IV

PHYSICAL CONSTANTS OF CHLORO-BROMOBUTANES

B.P./75 Mm., °C.	n_D^{20}	Believed to Be:
68.4–68.7	1.4670	1-Chloro-1-bromobutane
73.2–73.3	1.4788	1-Chloro-2-bromobutane
82.9–83.0	1.4770	1-Chloro-3-bromobutane

TABLE V

PHYSICAL CONSTANTS OF DICHLOROPROPANES

Compound	B.P., °C. Found	B.P., °C. Lit.	n_D^{20} Found	n_D^{20} Lit.
1,1	88.0	85.0–88.0	1.430	1.4288
1,2	97.4	96.4–96.8	1.4396	1.4388
1,3	121.2	119.0–120.4	1.4500	1.4487

TABLE VI

PHYSICAL CONSTANTS OF DICHLOROPROPANES

Compound	B.P., °C. Found	B.P., °C. Lit.	n_D^{20} Found	n_D^{20} Lit.
1,1	87.0–90.0	85.0–88.0	1.430	1.4288
1,2	96.1–96.2	96.4–96.8	1.4393	1.4388
1,3	119.7	119.0–120.4	1.4488	1.4487

No trichlorides were found. Yield about 56 percent.

was distilled. Of the three compounds isolated, the first (presumably 1,1-dichloropropane) could not be obtained in pure state. Comparisons of the physical constants of the dichlorides obtained in this study with those reported in the literature established their identities. The high-boiling products (24 g.) were not examined further.

Chlorination of n-propyl chloride in the liquid phase at −78°. For purposes of comparison, *n*-propyl chloride was chlorinated at −78° in the apparatus shown in Figure 2. *n*-Propyl chloride (707 g.) was placed in the flask, immersed in the Dewar flask in a Dry Ice-bath, where it was allowed to come to thermal equilibrium. Chlorine gas mixed with nitrogen gas then was passed into the propyl chloride. The stirrer was operated at high speed and the reaction was allowed to run until about 25 g. of chlorine had been consumed. The reaction mixture was warmed to room temperature and transferred to a distilling flask, where the excess of the propyl chloride was removed. In the meantime, another quantity of *n*-propyl chloride was chlorinated by the same procedure. The strippings from the first chlorination then were chlorinated again. Altogether, the procedure was repeated five times. The combined reaction products were distilled. Three fractions were obtained. The physical contants of these fractions are given in Table VI.

SUMMARY

1. The following products were obtained in the photobromination of alkyl halides at 100°:
   a. Ethyl bromide at 200° gave ethylidene bromide (86% yield).
   b. *n*-Propyl bromide gave propylene bromide (71%) and 1,2,3-tribromopropane (18%).
   c. Isopropyl bromide gave 2,2-dibromopropane (85% yield).
   d. *n*-Propyl chloride gave 1-chloro-1-bromopropane and 1-chloro-2-bromopropane in equal amounts (45% of each).
   e. *n*-Butyl bromide gave 1,2-dibromobutane and 1,3-dibromobutane in the ratio of 2:1, as well as substantial amounts of tri- and tetra-bromides.
   f. *sec*-Butyl bromide gave 2,2-dibromobutane and 2,3-dibromobutane in the ratio of 2:3, as well as large amounts of tri- and tetra-bromides.

g. *n*-Butyl chloride gave 1-chloro-1-bromobutane, 1-chloro-2-bromobutane, and 1-chloro-3-bromobutane in the ratio of 1:1:2.

h. *sec*-Butyl chloride gave 2-chloro-2-bromobutane (80%).

2. The photochlorination of propyl chloride at −78° and 100° gave 1,1-dichloropropane, 1,2-dichloropropane, and 1,3-dichloropropane in the ratio of 1:6:3, with slight variations, depending on the temperature of the reaction mixture.

3. An hypothesis to account for the products formed in bromination of alkyl halides is presented.

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NOTICE TO AUTHORS

On and after September 1, 1955, the Journal will accept *Notes*; the Journal will accept *Communications to the Editor* received on or after November 1, 1955 for publication in Volume 21. See revised Notice to Authors for details.

Effective with Volume 21, the Journal will use a double column format with a page size approximately 6½" by 9". Authors should consider this in connection with graph sizes, and table compositions.