tion, the viscosity average is bound to give distinctly larger molecular weights than the counting of the end-groups. This may explain the high bromine content of the polymer prepared at 217° (sample 116-E) where the decomposition of the catalyst should be expected to be very fast and at the same time thermal activation would be most efficient.

Acknowledgment

The authors are anxious to express appreciation to the directors of the Stamford Research Laboratories of the American Cyanamid Company for extending to the junior author the use of the laboratories' facilities. Thanks are also extended to the staff of the Columbia University cyclotron for bombardment of the samples.

Summary

1. Styrene has been polymerized in the pure liquid phase at various temperatures and with various amounts of *p*-bromobenzoyl peroxide.

2. The bromine content of the polymer was determined gravimetrically and with the aid of a radioactive bromine isotope. The values obtained by the two methods agreed reasonably well with each other.

3. The polymers contain on the average between one and three bromine atoms per chain, if the viscosity average chain length is compared with the analytical bromine content.

4. It is shown that the radioactive tracer method can be fairly easily applied to this problem of polymer chemistry.

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[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

Rearrangement of Alkyl Halides[1]

BY FRANK R. MAYO[2a] AND ARTHUR A. DOLNICK[2b]

The addition of hydrogen bromide to a 1-alkene may yield either of two products, depending on the mechanism of addition.[3] The normal addition, giving a secondary or tertiary bromide, proceeds by an ionic or molecular mechanism. The abnormal addition, which is accelerated by oxygen and peroxides and is inhibited by certain antioxidants, proceeds by an atom-chain mechanism, giving a primary bromide. On the assumption that the rearrangement of an alkyl bromide proceeds by loss and readdition of hydrogen bromide, it was concluded that the rate of rearrangement should be affected by the same catalysts which influence the addition of hydrogen bromide. This paper describes the effects of such catalysts on the rearrangement of normal and isopropyl bromides to an equilibrium mixture. These readily available bromides were chosen because the carbon skeleton cannot rearrange and because a mixture of the halides is easily analyzed. For comparison with a representative pair of alkyl chlorides, experiments were made with *i*- and *t*-butyl chlorides. Data were also obtained on the two dibromoethanes.

Previous Work

When an alkyl bromide is strongly heated, it rearranges to give an equilibrium mixture of all the isomeric bromides which can be formed without rearrangement of the carbon skeleton. In spite of considerable work in the field, there is marked disagreement on the composition of some equilibrium mixtures, on the factors which influence the rate of approach to equilibrium, and on the mechanism of rearrangement.

In the liquid phase at 250°, normal and isopropyl bromides rearrange to give a mixture containing 30 and 70%, respectively, of these bromides.[4a] The proportion of primary bromide increases with the temperature[4a] and is smaller in the vapor phase.[4b] Equilibria between tertiary and isobutyl bromides have been more extensively investigated[5] in both the liquid and the vapor phase, but although the tertiary bromide always predominates, wide discrepancies in the composition of the equilibrium mixture have been reported; secondary butyl bromide (with rearrangement of the carbon skeleton) has also been detected.[5g] Equilibria between the four bromoisopentanes and between some isomeric dibromoalkanes have received less attention.[5a,6]

The rearrangement of the bromoisobutanes is retarded by the corresponding alcohols and by di-isobutylene.[5b] Michael has recently suggested[7]

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(2) Present addresses: (a) General Laboratories, United States Rubber Company, Passaic, N. J.; (b) Publicker Commercial Alcohol Company, Philadelphia, Pa.

(3) Mayo and Walling, *Chem. Rev.*, **27**, 351 (1940).

(4) (a) Brouwer and Wibaut, *Rec. trav. chim.*, **53**, 1001 (1934); (b) Brunel and Rafsky, *Science*, **60**, 23 (1924).

(5) (a) Michael and Leupold, *Ann.*, **379**, 263 (1911); (b) Michael, Scharf, and Voigt, THIS JOURNAL, **38**, 653 (1916); (c) Brunel, *Ber.*, **44**, 1000 (1911); (d) Brunel, *Ann.*, **384**, 245 (1911); (e) Brunel, THIS JOURNAL, **39**, 1978 (1917); (f) Dienger, *Z. physik. Chem.*, **136**, 93 (1928); (g) Hückel and Ackermann, *J. prakt. Chem.*, [2] **136**, 15 (1933).

(6) (a) Gustavson, *J. prakt. Chem.*, [2] **36**, 303 (1887); (b) Faworsky, *et al.*, *Ann.*, **354**, 325 (1907); (c) Michael and Zeidler, *ibid.*, **385**, 227 (1911).

(7) Michael, *J. Org. Chem.*, **4**, 521 (1939), footnote 9.

that his earlier work[5a,b] shows an acceleration by oxygen. Aluminum,[6a,8b,d] zinc and mercuric[5b] bromides accelerate the rearrangement of several bromides. There is disagreement as to whether rearrangement is faster in the vapor than in the liquid phase[5a,b,e,8a] and as to the effect of various surfaces on the rate of rearrangement.[5a–c,6c] Difficulty in reproducing results has been mentioned frequently; catalytic effects have seldom been demonstrated by duplicate experiments, and frequent discrepancies between workers suggest that many conclusions are open to question. Typical of the state of the subject are the repeated claims,[5a,c,f,6c,8c] often refuted,[5e,6b,8f] that equilibrium is approached much faster from one side than from the other, that it can be approached only from one side, and that impurities[5b] determine the composition of the equilibrium mixture.

Rearrangement through loss and readdition of hydrogen bromide has been postulated,[4a,5d,6b,8a–c,9a] while those who favor an intramolecular rearrangement base their contentions upon failure to observe dissociation sufficient to account for rearrangement.[5a,b,f,g,8e,9b]

Alkyl chlorides, which rearrange with difficulty, have received comparatively little attention.[10]

Experimental

Conditions for Isomerization.—Generally, the propyl bromide[11] (3 cc. measured at room temperature) was heated for six hours at 250° in a sealed, heavy-walled, Pyrex tube (5.7 mm. inside diameter, 35 cm. long, 8–9 cc. capacity), enclosed in a close-fitting iron pipe. In runs where air was excluded, measured quantities of the dried bromide were distilled *in vacuo* into the cooled reaction tube containing the catalyst (if any), and sealed off (final pressure 10^{-4} mm. or less). When hydrogen bromide or propene was added, it was measured out in the vapor phase and condensed in the reaction vessel. For runs in the presence of air, the halides were pipetted into cooled (−80°) tubes and sealed off.

In the first third of the experiments, the reaction tubes were heated in a horizontal electric furnace, but when it was found that the temperature varied from 250° at the center to 210° at the ends of the tubes, the remaining experiments were carried out in boiling diphenyl ether (temperature 248–252°).[12] Tubes were introduced into the preheated furnace or bath; they attained the maximum temperature within fifteen minutes in the diphenyl ether-bath, more slowly in the furnace. In most of the experiments, the two methods of heating gave nearly identical results, but the runs without added catalysts or air tend to fall into two groups (Fig. 1). Less rearrangement was found in the electrically heated runs, ten out of eleven products having indices of refraction between 1.4328 and 1.4332. The halide presumably rearranged faster in the diphenyl ether-bath experiments because the temperature was higher and more rapidly attained.

Analysis of Reaction Products.—The heated tubes were cooled to −80° and opened. The products (usually colorless but containing hydrogen bromide) were washed several times with water, with concentrated sulfuric acid, and again with water. The percentage composition of the halide mixture (dried over potassium carbonate) was then estimated by determination of the index of refraction.[13] The analytical procedure was proved applicable by tests with known mixtures. It was found unnecessary to distil the rearrangement products of *n*-propyl bromide[14] except that those formed in the presence of aluminum bromide, catechol, or diphenylamine were vacuum-distilled before washing. In the experiments with bromobenzene, the bromopropanes were separated before washing by fractionation through a short Vigreux column. This procedure was found adequate with a known mixture. The chloroisobutanes were merely distilled before their refractive indices were determined. Because the dibromoethanes partially decomposed to hydrogen bromide and a black solid (amounting to about 15% of the product), the volatile products were distilled *in vacuo*, dried with anhydrous potassium carbonate, and fractionated through a small Vigreux column. Material boiling below 105° (mostly at 40–51°, probably ethyl and vinyl bromides) was rejected; the composition of the fraction boiling at 105–132° was determined by index of refraction.[15] Residue and hold-up were negligible.

Reagents.—One preparation of *n*-propyl bromide (made from *n*-propanol[16]), having the usual physical properties, rearranged unusually rapidly and was found to contain peroxides. This sample was washed with 2% aqueous potassium permanganate until no more reduction occurred; it was then washed until colorless with concentrated sulfuric acid. After treatment with aqueous potassium carbonate and then with water, the dried and distilled propyl bromide rearranged at the usual rate. Thereafter, all the propyl bromide (b. p. 749 mm. 70–71°, $n^{20}\mathrm{D}$ 1.4341), from which about 75% of the runs were made, was treated in this manner. Isopropyl bromide (Eastman Kodak Co.) was washed with concentrated sulfuric acid and water, dried and fractionally distilled; b. p. 747 mm. 58.5–59.0°, $n^{20}\mathrm{D}$ 1.4251. *t*-Butyl chloride,[17a] b. p. (739 mm.) 49.5°, $n^{20}\mathrm{D}$ 1.3853, and isobutyl chloride,[10a,17b] $n^{20}\mathrm{D}$ 1.3974, were prepared from the corresponding alcohols.

Catechol and diphenylamine were sublimed at reduced pressure; *n*-propanol, di-isopropyl ether, and bromobenzene were fractionally distilled. Anhydrous aluminum bromide was prepared from aluminum and reagent grade bromine[18] and stored and transferred in a dry atmosphere. The colorless salt dissolved rapidly and completely in alkyl halides with discoloration and development of heat.

Results

Rate Studies.—Since the equilibrium between the bromopropanes at 250° lies on the side of the secondary halide, isomerization of *n*-propyl bromide to the equilibrium mixture results in a greater change in composition and refractive index than would occur with its isomer. Conse-

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(8) (a) Eltekoff, *Ber.*, **8**, 1244 (1875); (b) Kekulé and Schrötter, *ibid.*, **12**, 2279 (1879); (c) Aronstein, *Rec. trav. chim.*, **1**, 134 (1882); (d) Gustavson, *Ber.*, **16**, 958 (1883); (e) Ramart-Lucas and Salmon-Legagneur, *Compt. rend.*, **186**, 39 (1928); (f) Bethoud and Porret, *J. chim. phys.*, **30**, 396 (1933).

(9) (a) Meerwein and van Emster, *Ber.*, **55**, 2520 (1922), footnote; (b) Eltekoff, quoted in reference 6b.

(10) (a) Michael and Zeidler, *Ann.*, **393**, 81 (1912); (b) Nagai, *C. A.*, **34**, 7844 (1940).

(11) Ethylene and ethylidene bromides were heated in tubes which were about three-quarters filled.

(12) A temperature of 300° for the chloroisobutane experiments was obtained by the use of boiling benzophenone.

(13) Kharasch, McNab and Mayo, THIS JOURNAL, **55**, 2531 (1933); Kharasch and McNab, *ibid.*, **56**, 1425 (1934).

(14) Distillation caused an inconsistent change in refractive index of 0.0002 or less. The absence of significant amounts of by-products was shown by distillation of the accumulated rearrangement products (700 g.), which yielded about 1 g. of material boiling below 58° and about 3 g. boiling above 70°.

(15) Kharasch, McNab and Mayo, THIS JOURNAL, **55**, 2521 (1933).

(16) Carothers, "Organic Syntheses," Vol. 13, John Wiley and Sons, Inc., New York, N. Y., 1933, p. 21.

(17) (a) Gilman, "Organic Syntheses," Coll. Vol. 1, John Wiley and Sons, Inc., New York, N. Y., 1932, p. 138; (b) Gerrard, *J. Chem. Soc.*, 99 (1939).

(18) Winter and Cramer, *Ind. Eng. Chem.*, **32**, 856 (1940).

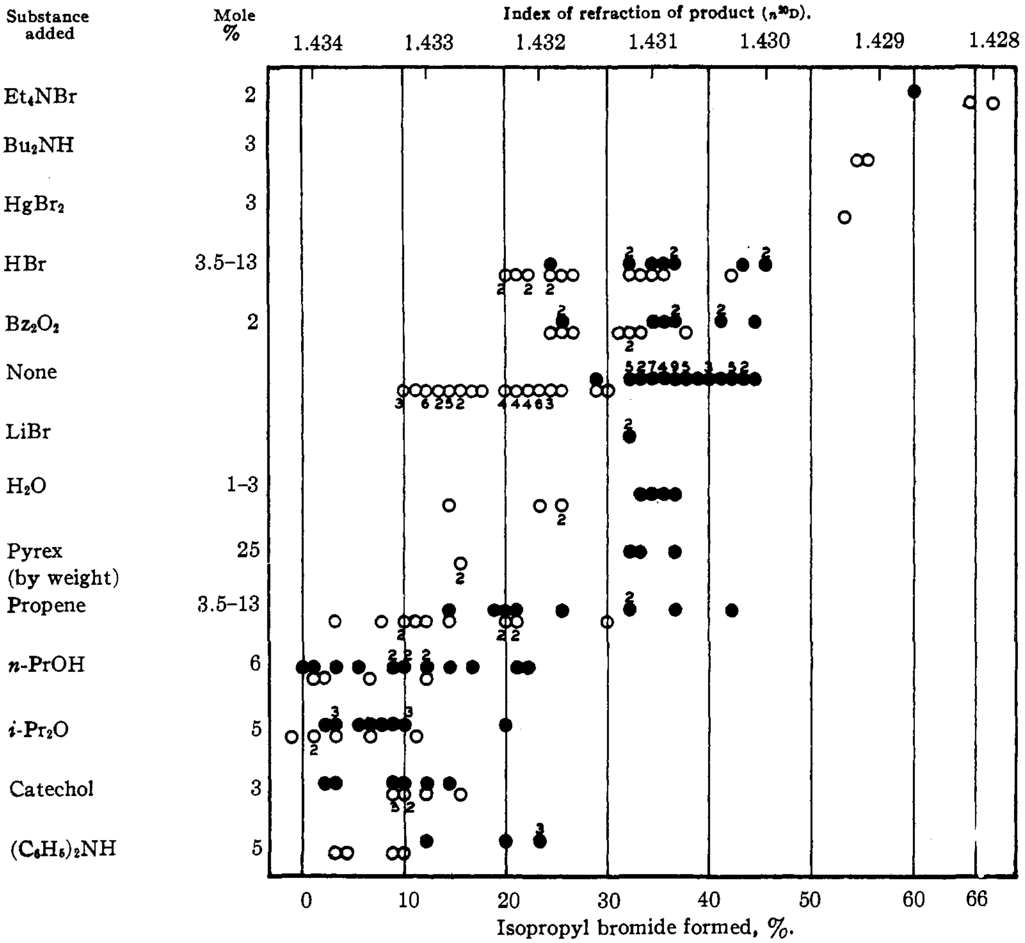

Fig. 1.—Extent of rearrangement of *n*-propyl bromide after six hours at 250°. Hollow circles represent experiments made in the absence of air; solid circles indicate presence of air. A number above or below a point shows the total number of duplicate experiments which gave the indicated result. The equilibrium mixture contains 66–67% isopropyl bromide.

quently, rate studies were carried out by heating the liquid primary bromide for six hours at 250°. Results are summarized in Fig. 1.

Oxygen and Peroxides; Precision of Results.—In the absence of air at 250°, 9–30% of *n*-propyl bromide rearranges during six hours to the secondary halide (Fig. 1), whereas 67% represents equilibrium. Using the same *n*-propyl bromide for each set, eight pairs of duplicate experiments gave products having a maximum difference in index of refraction of 0.0002 (2.2%) within each pair; hence catalytic impurities in the halides and the method of heating are probably responsible for the wide differences in the results obtained.

While the values actually overlap slightly, the rearrangement of *n*-propyl bromide (29–43%) is unmistakably faster in the presence of air than in its absence. Whenever air and air-free experiments were made simultaneously from the same sample of *n*-propyl bromide, 11–25% (average 17%) more rearrangement was always obtained in the presence of air. Hence the overlapping of air and air-free runs shown in Fig. 1 is due to variations in the *n*-propyl bromide or in heating. Oxygen is responsible for the accelerating effect of air: in simultaneous experiments, 9% rearrangement was found in a vaccum run, 18% and 42% were found after bubbling commercial nitrogen and oxygen, respectively, through the bromide samples before the reaction tubes were sealed. Air was also found to accelerate the rearrangement of isopropyl bromide.

Experiments with benzoyl peroxide yielded some charred material and erratic results. In view of the short life of the peroxide above 100°, the results are not considered to be significant.

Bromide Salts.—The powerful catalytic effect of aluminum bromide, which caused extensive side-reactions at elevated temperatures, was demonstrated by equilibrium studies at low temperatures. Addition of 2 mole % of tetraethylammonium bromide to reaction mixtures resulted in close approach to equilibrium (67% rearrangement) in six-hour runs at 250°;[19] mercuric bro-

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[19] Only 17% rearrangement was found in the same time at 200°.

mide and dibutylamine were only slightly less effective. The effect of dibutylamine is almost certainly due to its conversion to an alkylammonium bromide since colorless, water-soluble crystals were obtained from reaction mixtures to which this amine had been added. Lithium bromide had no effect, but it was apparently insoluble. Tetraethylammonium bromide also accelerated the rearrangement of isopropyl bromide.

Hydrogen Bromide and Propene.—Because of variations in the propyl bromide, it is necessary to compare runs made simultaneously with and without hydrogen bromide, in order to demonstrate the accelerating effect of this substance. In air-free runs, experiments with hydrogen bromide never showed less, and usually showed more, rearrangement than the corresponding blanks; when more than 10 mole % of the acid was added, 10–15% more isopropyl bromide was always formed than in the blank. In air runs, a similar acceleration was observed only at high hydrogen bromide concentrations; there was no consistent effect at low concentrations. Hydrogen bromide also accelerates rearrangement in the presence of catechol. Two air-free runs, each containing 3 mole % of catechol, were made up, to one of which 15 mole % of hydrogen bromide was added. The run without hydrogen bromide gave 10% rearrangement; the other gave 34% rearrangement. A large effect of hydrogen bromide should not be anticipated since it always appeared ($^1/_3$ to 5 mole % in air-free runs, $^1/_3$ to 2 mole % in air runs) in experiments, even when none had been added.

A small retarding effect of added propene can be shown in both the presence and absence of air. In ten experiments with added propene accompanied by simultaneous blank runs, nine rearranged 2–18% less (average 11%) than the blank, but a definite relation between the amount of alkene and the extent of rearrangement is not discernible.

Inhibitors.—Experiments with added catechol show that this antioxidant completely overcomes the accelerating effect of air on the rearrangement and reduces the effects of accidental catalysts in the *n*-propyl bromide. When simultaneous experiments were made with catechol, the air and air-free runs were identical (four pairs of experiments). In four pairs of experiments in the absence of air, the inhibitor had a marked retarding effect (12–16% rearrangement) only when the blanks rearranged rather rapidly (23% rearrangement), a slight effect when the blanks rearranged slowly (9–10% rearrangement). Diphenylamine proved to be a less effective inhibitor.

Figure 1 shows that *n*-propanol is also a fairly effective inhibitor. Di-isopropyl ether is the most effective; in the absence of air, it sometimes stops rearrangement completely. No allowance has been made in analyses for the possibility that these two inhibitors may have been partly converted to bromopropanes.

Conditions without Significant Effects.—Addition of 1 to 3 mole % of water or 25% by weight of crushed Pyrex glass (average size about 30 mesh) had no significant effect on the rate of rearrangment. Whether the reaction tubes were cleaned by strong heating in an air stream or by treatment with chromic–sulfuric acid mixture was also unimportant. Illuminating *n*-propyl bromide in an open quartz tube with a mercury vapor lamp for one hundred forty hours at room temperature produced discoloration, 1.5 mole % of hydrogen bromide, and high-boiling material, but no isopropyl bromide. Rearrangement of isobutyl bromide by ultraviolet light has been reported.[8e]

Rearrangement in the Vapor Phase and in Solution.—In the experiments summarized in Fig. 1, the reaction tubes were one-third filled with liquid propyl bromide at room temperature, about two-thirds filled at 250°. Decreasing the free space above the liquid had little effect on the rate of rearrangement, but with sufficient space to permit complete vaporization of the propyl bromide (tubes 2% filled at room temperature), less than 1% rearrangement occurred in the absence of air. This retardation is not due simply to dilution, for in tubes 2% filled with propyl bromide and two-thirds filled with bromobenzene (of essentially the same dielectric constant), rearrangement (17–26%) proceeded as in liquid-phase, air-free runs without solvents. However, eight vapor-phase rearrangements in the presence of air gave 12–31% (mean, 20%) rearrangement, just half the average of simultaneous liquid-phase blanks with air in small tubes. In six bromobenzene experiments with air present, 12–42% (mean, 25%) rearrangement was found.

Equilibrium between *n*- and Isopropyl Bromides.—As shown in Fig. 2, the same equilibrium mixture (containing 67% isopropyl bromide as compared with 70% reported by Brouwer and Wibaut[4a]) was obtained at 250° from both *n*- and isopropyl bromides, regardless of the presence or absence of tetraethylammonium bromide or air. With these catalysts, equilibrium could not be obtained within a reasonable time at or below 200°. Aluminum bromide could not be used at 250°, but gave equilibrium mixtures containing 85% isopropyl bromide at 70°, 91% at 26°.

Rearrangement of *i*- and *t*-Butyl Chlorides.—Isobutyl and *t*-butyl chlorides were unchanged after six hours at 250°, but each gave about 10% rearrangement in seven hours at 300°. Neither catechol nor air affects the rearrangement of isobutyl chloride. About 26% of this chloride rearranged in fifteen hours at 300°, in the presence or absence of air and/or 3 mole % of catechol. On the other hand, addition of 3 mole % of triethylammonium chloride increased rearrangement of isobutyl chloride to 78 during seven hours at 300°. The equilibrium mixture apparently contains between 78 and 92% of tertiary chloride, but the value is uncertain due to the formation of considerable high-boiling material in runs starting with *t*-butyl chloride.

Rearrangement of Ethylene and Ethylidene Halides.—Ethylene and ethylidene chlorides were boiled with 2 mole % of aluminum chloride; ethylene bromide was refluxed with 1 mole % of aluminum bromide, and ethylidene bromide was heated to 100° in a sealed tube with 4 mole % of aluminum bromide. No rearrangement was observed over periods of six and one-half to ninety-four hours, but considerable halogen exchange occurred when ethylene chloride was refluxed with 23 mole % of aluminum bromide. Rearrangement of the dibromoethanes with aluminum bromide at higher temperatures was unsuccessful because of the large amount of tar formed, but less side reaction occurred when either dibromide was heated for twenty-eight to thirty-two hours at 250° with 4–5 mole % of tetraethylammonium bromide. Two experiments were carried out with each dibromoethane; the four products were found to contain 76–82% of ethylene bromide, 18–24% of ethylidene bromide.

Discussion

Correlation with Previous Work.—The present work supports the previous statements that rearrangement of alkyl bromides is accelerated by air and some metal bromides, and is retarded by alcohols and alkenes. With reference to previously disputed points, this paper shows that the rearrangement is much slower in the vapor than in the liquid phase, that there is no surface effect from glass, that reproducibility of results is highly dependent on catalysts and inhibitors present as impurities in the alkyl bromide, and that equilibrium can be approached from both sides. The analogies discussed below, as well as the formation of free hydrogen bromide in all experiments, point to rearrangement by loss and readdition of hydrogen bromide rather than by an intramolecular mechanism.

The Mechanisms of Rearrangement of Alkyl Halides.—Addition of hydrogen bromide to propene may occur by either of two mechanisms, each associated with different catalysts and each leading to a different propyl bromide.[3] Loss of hydrogen bromide from an alkyl bromide presumably occurs by the reverse processes. The present observations on the rate of rearrangement of the bromopropanes are entirely consistent with the view that rearrangement consists of loss and readdition of hydrogen bromide by the same two mechanisms, but here the two mechanisms can be distinguished not by the products formed, but only by analogy with the addition reaction. On this basis, the accelerating effect of oxygen on the rearrangement of the bromopropanes, and the counteracting effect of antioxidants, are associated with the atom-chain mechanism of hydrogen bromide addition. The slight acceleration by hydrogen bromide and the greater effect of soluble bromide salts are associated with the normal, molecular mechanism of hydrogen bromide addition according to Markownikoff's rule. Substances which reduce the concentration of hydrogen bromide, such as propene, propanol and di-isopropyl ether, retard the rearrangement; the alcohol and ether may also retard the chain reaction. Since hydrogen chloride does not add to alkenes by the chain mechanism, both the absence of an oxygen effect and the presence of a catalytic effect of triethylammonium chloride are observed and expected.

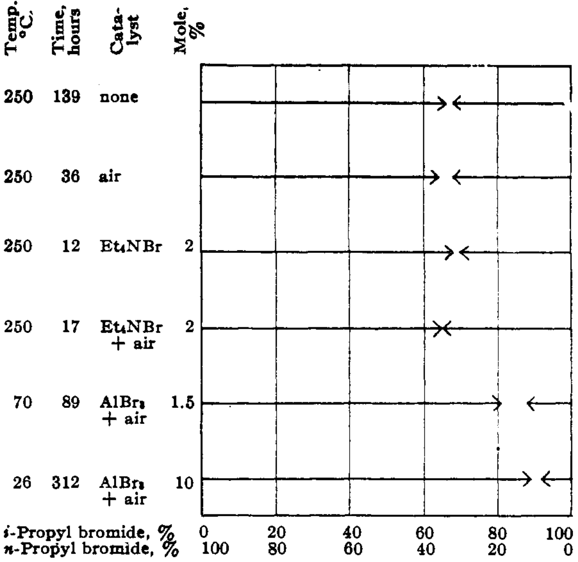

Fig. 2.—Liquid-phase equilibrium between *n*- and isopropyl bromides. Each line indicates the change undergone by a propyl bromide sample when heated under the stated conditions. The starting materials are indicated at the margins; the arrow heads show the final compositions. Experiments at 250 and 70° were carried out in sealed tubes; at 26°, open reflux condensers were used, with protection from moisture in the air.

As in many hydrogen bromide additions, the rearrangement of the bromopropanes seems to proceed by both mechanisms in the absence of air, as shown by the variable rates observed and their tendency to approach a lower limit in the presence of the antioxidant, catechol. The differences in the effectiveness of inhibitors, and the retardation or elimination of the molecular mechanism by diluting or operating in the vapor phase also have nearly identical counterparts in the addition reactions.[3]

Rates and Equilibria in the Formation and Rearrangement of Alkyl Bromides.—Hydrogen bromide adds rapidly to propene under ordinary conditions to give isopropyl bromide.[13] This isomer must be formed at least ninety-nine times as fast as *n*-propyl bromide since probably no more than 1% of the primary halide is present.

Similar results have been obtained in the cold in the presence of ferric chloride,[20] and presumably the same product would be obtained in a short time with aluminum bromide as catalyst. However, it is now shown that aluminum bromide, in a few hours at room temperature, converts either bromopropane to an equilibrium mixture containing 91% isopropyl bromide. Hence if isopropyl bromide is formed from propene and hydrogen bromide at least ninety-nine times as fast as normal propyl bromide, the secondary bromide must dissociate at least ten times as fast as the primary bromide, in order to account for the equilibrium. Thus the usual formation of isopropyl bromide in the addition reaction is due to the fact that addition is complete long before equilibrium is established. Since both mechanisms of addition and rearrangement lead to the formation of the same equilibrium mixture, addition by the normal mechanism must always give at least a little of the *n*-propyl bromide; addition by the chain mechanism must always give some isopropyl bromide; and any catalyst which preferentially accelerates formation of one bromopropane must also preferentially favor the dissociation of the same bromopropane.

From the liquid-phase equilibrium data for normal and isopropyl bromides (the equilibrium mixture containing 91% of isopropyl bromide at 26°, 67% at 250°), calculation shows that the isomerization of primary to secondary halide evolves 2.2 kcal./mole.[21] Conn, Kistiakowsky and Smith[22] have justified the Markownikoff rule for the addition of halogen acids to alkenes because it predicts the formation of the thermodynamically more stable alkyl halides. While this generalization may well be correct for unsaturated hydrocarbons, it does not apply to vinyl bromide. Although in this case the normal addition of hydrogen bromide yields almost exclusively ethylidene bromide in the liquid phase at room temperature[15] or 100°,[23] or in the vapor phase at 200°,[23] the equilibrium mixture at 250° contains about 80% of ethylene bromide. Thus, here the abnormal addition yields the more stable of the two possible products.

The Redistribution Reaction.—Ethyl chloride and ethylene bromide react at room temperature in the presence of aluminum chloride to give a mixture containing ethyl bromide, ethylene chloride, ethylene chlorobromide, and the original halides.[24] Since it has now been shown that aluminum chloride does not rearrange the dichloro- and dibromoethanes below their boiling points, while replacement of one halogen by another occurs easily, the redistribution reaction of Calingaert, *et al.*, must involve a displacement reaction,[25] not loss and readdition of hydrogen halides.

Summary

The liquid-phase rearrangement of the bromopropanes to an equilibrium mixture has been studied. Many analogies between this reaction and the addition of hydrogen bromide to alkenes suggest that rearrangement of an alkyl bromide occurs by loss and readdition of hydrogen bromide and that the reactions proceed by two mechanisms. The first of these is a non-chain mechanism accelerated by soluble bromide salts or hydrogen bromide and retarded by substances which remove hydrogen bromide. The second is an atom-chain mechanism accelerated by oxygen and inhibited by antioxidants. Alkyl chlorides rearrange by the non-chain mechanism.

Since rearrangement of either propyl bromide is accelerated by catalysts for both mechanisms, the commonly observed formation of a single addition product from a halogen acid and an alkene is due to the fact that the first-formed addition product rearranges very slowly. Although the non-chain addition (in accord with Markownikoff's rule) usually yields the thermodynamically more stable isomer, the addition of hydrogen bromide to vinyl bromide is exceptional.

With the dihaloethanes, the replacement of one halogen by another in the presence of aluminum chloride or bromide proceeds much more easily than rearrangement.

PASSAIC, N. J. RECEIVED MARCH 17, 1944

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(20) Kharasch, Kleiger and Mayo, *J. Org. Chem.*, **4**, 428 (1939).

(21) Errors of 2% in the composition of the equilibrium mixtures would lead to a maximum error of 0.4–0.5 kcal./mole in the heat of isomerization. The heat effect for the vapor-phase isomerization can be calculated as 2.9 kcal./mole from the heats of hydrogenation and bromination of alkenes, Kistiakowsky, Ruhoff, Smith and Vaughan, THIS JOURNAL, **57**, 876 (1935).

(22) Conn, Kistiakowsky and Smith, *ibid.*, **60**, 2764 (1938).

(23) Wibaut, *et al.*, *Rec. trav. chim.*, **50**, 313 (1931). The maximum recorded yield of ethylidene bromide is assumed to approach most closely the composition of the normal addition product, for the most probable side-reactions (abnormal addition and rearrangement) tend only to increase the proportion of ethylene bromide.

(24) Calingaert, Soroos, Hnizda and Shapiro, THIS JOURNAL, **62**, 1545 (1940).

(25) Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 131.