The authors gratefully acknowledge their indebtedness to the Jackson Laboratories of E. I. du Pont de Nemours and Co. for a generous supply of ethylmercury chloride.

## Summary

1. It has been found that alkyl and aryl mercury halides in alkaline solution react with acetylene with the formation of soluble mercury acetylides of the general formula R—Hg—C≡C—Hg—R.

2. The acetylene derivatives of methyl, ethyl, *n*-propyl, *n*-butyl, *n*-amyl, *n*-hexyl, phenyl, *o*-tolyl, *p*-tolyl and benzylmercury halides have been prepared and their properties recorded.

3. Since these acetylenic derivatives are easily prepared and purified and possess sharp melting points, they are suitable derivatives for the identification of organo-mercury halides.

NOTRE DAME, INDIANA

RECEIVED NOVEMBER 12, 1932
PUBLISHED JUNE 6, 1933

---

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

# The Peroxide Effect in the Addition of Reagents to Unsaturated Compounds. I. The Addition of Hydrogen Bromide to Allyl Bromide

BY M. S. KHARASCH AND FRANK R. MAYO[1,2]

## Introduction

The theory of partial polarity of the ethylene bond proposed by one of us[3] postulates that in unsymmetrical ethylene compounds, one of the two electron pairs constituting the double bond is held in common by the two carbon atoms concerned and the other behaves as if it were decidedly closer to one of the carbon atoms than to the other. It is an essential part of the theory also that this second electron pair lies closer in general to that carbon atom which carries the least electronegative radicals. In view of some discrepancies between the predicted and the experimentally recorded results, it became necessary to repeat the work on the addition of hydrogen bromide to allyl bromide and many other unsaturated compounds. In the course of this work, the effect of peroxides on the direction of addition was discovered. This paper deals with the magnitude of that effect on the addition of hydrogen bromide to allyl bromide, but

---

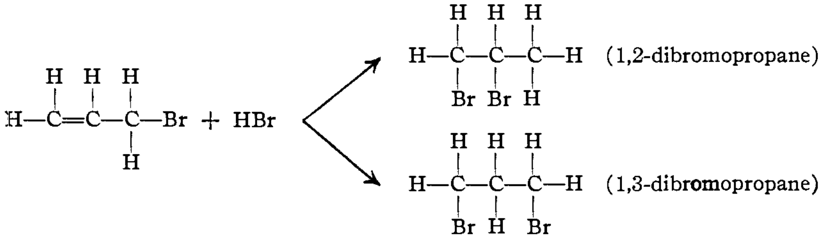
[1] This communication is an abstract of a dissertation submitted by Frank R. Mayo in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry at the University of Chicago, 1931. A part of this work was presented at the Cincinnati meeting of the American Chemical Society, September, 1930.

[2] The authors wish to take this opportunity to express their appreciation to the Eli Lilly Company of Indianapolis for support which made this work possible.

[3] Kharasch and Darkis, *Chem. Rev.*, **5**, 571 (1928); Kharasch and Reinmuth, *J. Chem. Education*, **8**, 1703 (1931).

observations made on other systems show clearly that the results obtained in the case under discussion have a wide applicability, the limits of which have not yet been determined.

Hydrogen bromide may add to allyl bromide in two different ways



Both reactions have been noted many times and a copious literature exists on the various physical and chemical influences which may cause the addition to proceed in one way or the other.[4] In the light of our findings, all of these results need reinterpretation, for seldom were any of the workers evaluating one factor at a time.

Obviously, no discussion of the results of an addition of hydrogen bromide to allyl bromide can be of much significance unless there exists a fairly satisfactory method for the quantitative analysis of the resulting mixture. We have found the analytical methods in existence unsatisfactory and have evolved a method which enables us to determine the percentage composition of a mixture of the two dibromides concerned with a precision of five per cent. The analytical methods employed, the technique of addition under definitely controlled conditions, as well as the demonstration that no rearrangement of allyl bromide or the addition products occurs during the addition, are described in the experimental part.

## Factors Influencing the Addition of Hydrogen Bromide to Allyl Bromide

**1. The Peroxide Effect.**[5]—The following observations convinced us that there were still unsuspected factors which influenced the addition under investigation. If the addition is carried out *in vacuo*,[6] different samples of allyl bromide reacted with varying velocities to give different proportions of addition products (Table I). In the majority of these runs, the product of the addition was 65–85% 1,2-dibromopropane and an

---

[4] Geromont, *Ann.*, **150**, 369 (1871); Reboul, *Compt. rend.*, **74**, 614 (1872); **76**, 1270 (1873); Lermontoff, *Ann.*, **182**, 358 (1876); Bogomolez, *Ber.*, **11**, 1257 (1878); *Bull. soc. chim.*, [2] **30**, 23 (1878); Reboul, *Ann. chim.*, [5] **14**, 470 (1878); Erlenmeyer, *Ann.*, **197**, 169 (1879); Roth, *Ber.*, **14**, 1351 (1881); Niederist, *Monatsh.*, **3**, 838 (1882); Bruylants, *Rec. trav. chim.*, **28**, 246 (1909); Böeseken, *ibid.*, **34**, 99 (1915); **37**, 260 (1918); Holleman and Matthes, *Proc. Acad. Sci. Amsterdam*, **21**, 90 (1918); Frankel and Kuk, *Biochem. Z.*, **226**, 223 (1930); Clark and Gray, *Trans. Roy. Soc. Can.*, [3] **24**, Sect. 3, 111 (1930); Wibaut, *Rec. trav. chim.*, **50**, 313 (1931).

[5] All of the experiments of which the results are reported in this section were made in the dark at room temperature in the absence of solvents.

[6] In these papers, the expression *in vacuo* will indicate that while the reaction mixtures were frozen solid at the temperature of liquid air, residual gases in the bomb tubes were removed by evacuation before the tubes were sealed off. Naturally there was no vacuum, but pressure, in the tubes when the reaction mixtures warmed up. For further details, consult the experimental part.

average of 88% of the allyl bromide reacted in ten days.[7] Reaction occurred much more rapidly in the remaining runs in which 1,3-dibromopropane was the principal product. That this variation in both yield and product was due to some sort of oxygen or peroxide effect is indicated by a consideration of the results of Table II. As long as the reaction was run in the presence of air or oxygen, as many as fifteen samples of allyl bromide reacted alike and yielded almost entirely (87 ± 5%) 1,3-dibromopropane in a comparatively rapid reaction. In at least one of these runs (No. 172) the addition was complete within an hour.

TABLE I

THE ADDITION OF HYDROGEN BROMIDE TO ALLYL BROMIDE IN THE DARK AT ROOM TEMPERATURE IN THE ABSENCE OF SOLVENTS AND GASES[a]

| No. | Yield, % | Reaction time | % 1,3-[b] | Remarks |
|---|---|---|---|---|
| 135 | 86 | 9 days | 32 | |
| 160 | 94 | 11 days | 33 | |
| 161 | 95 | 11 days | 29 | |
| 181 | 99 | 18 days | 87 | 1.25 moles HBr used |
| 182 | 100 | 8 days | 17 | 3.03 moles HBr used |
| 185 | 100 | 10 days | 83 | |
| 198 | 100 | 10 days | 71 | |
| 205 | 91 | 10 days | 18 | |
| 208 | 85 | 15 days | 28 | 1.21 moles HBr used |
| 212 | 88 | 9 days | 27 | Dried 3 hours with large excess $P_2O_5$ |
| 214 | 91 | 9 days | 24 | Dried 15 min. with small amount $P_2O_5$ |
| 233 | 87 | 10 days | 29 | Dried 4.5 hours |
| 234 | 87 | 10 days | 22 | Dried 15 min. |
| 258 | 85 | 9 days | 26 | |
| 259 | 83 | 9 days | 25 | |
| 277 | 96 | 9 days | 46 | |
| 278 | 87 | 9 days | 18 | |
| 350 | 100 | 12 days | 76 | |
| 361 | 79 | 10 days | 26 | |
| 443 | 82 | 10 days | 42 | |
| 362 | 75 | 10 days | 13 | Nitrogen passed through allyl bromide for ten minutes before solution of hydrogen bromide |
| 363 | 100 | 10 days | 74 | Same, but with oxygen instead of nitrogen |
| 137 | 78 | 9 days | 17 | Dried with $Na_2SO_4$ instead of $P_2O_5$ |
| 156 | 91 | 10 days | 24 | Dried with $Na_2SO_4$ instead of $P_2O_5$ |
| 164 | 93 | 10 days | 33 | Dried with $Na_2SO_4$ instead of $P_2O_5$ |
| 165 | 100 | 10 days | 71 | Dried with $Na_2SO_4$ instead of $P_2O_5$ |
| 184 | 96 | 10 days | 46 | Dried with $Na_2SO_4$ instead of $P_2O_5$ |
| 204 | 98 | 10 days | 15 | Dried with $Na_2SO_4$ instead of $P_2O_5$ |
| 407 | 76 | 9 days | 13 | Dried with $CaCl_2$ instead of $P_2O_5$ |
| 191 | 100 | 3 days | 84 | Dried with silica gel[c] instead of $P_2O_5$ |
| 203 | 100 | 6 days | 85 | Dried with silica gel[c] instead of $P_2O_5$ |

---

(7) It has been our experience that under peroxide-free conditions, the normal addition proceeds to the extent of about 35% the first day, 15% the second day, and more slowly thereafter so that a yield of 85–90% is obtained in ten days.

TABLE I (*Concluded*)

| No. | Yield, % | Reaction time | % 1,3-[b] | Remarks |
|---|---|---|---|---|
| 386 | 85 | 11 days | 11 | 0.011 mole hydroquinone present |
| 387 | 97 | 11 days | 11 | .014 mole diphenylamine present |
| 428 | 93 | 9 days | 11 | .014 mole mercaptobenzothiazole present |
| 442 | 98 | 10 days | 10 | .029 mole thiocresol present |
| 445 | 89 | 65 hours | 10 | .058 mole tertiary butyl isocyanide present |
| 200 | 76 | 4 days | 24 | Reaction mixture distilled *in vacuo* without drying |
| 207 | 87 | 9 days | 18 | |
| 232 | 100 | 10 days | 71 | |
| 222 | 92 | 10 days | 20 | Reaction mixture was not dried or distilled, but bomb tube was evacuated before sealing |
| 243 | 98 | 12 days | 66 | |
| 245 | 99 | 9 days | 83 | |
| 242 | 99 | 12 days | 84 | |
| 285 | 92 | 15 months | 26 | Saturated 11 times with HBr at −10°, but not dried, distilled or evacuated |

[a] Except as otherwise noted, these reaction mixtures were prepared according to the drying and distillation procedure described in the experimental part, and 1.5 moles of hydrogen bromide was used.

[b] The figures given in this column represent the percentage of 1,3-dibromopropane in the pure addition product. The remainder of the product is 1,2-dibromopropane.

[c] The large yields of 1,3-dibromopropane obtained with this drying agent are probably accounted for by the fact that the silica gel was not degassed before it was used.

TABLE II

THE ADDITION OF HYDROGEN BROMIDE TO ALLYL BROMIDE IN THE PRESENCE OF AIR OR OXYGEN[a]

| No. | Yield, % | Reaction time | % 1,3-[b] | Remarks |
|---|---|---|---|---|
| X10 | 99 | 5 days | 90 | Mean of three results |
| B2 | 100 | 5 days | 92 | Mean of two results |
| 172 | 100 | 1 hour | 90 | |
| 219 | 99 | 20 hours | 90 | Mean of two results |
| 244 | 100 | 9 days | 88 | (V)[a] undried air admitted, mean of two results |
| 415 | 100 | 18 hours | 82 | (V)[a] dried air admitted |
| 251 | 100 | 5 days | 84 | (V)[a] dried oxygen admitted, mean of four results |
| 369 | 87 | 8 days | 10 | 0.01 mole hydroquinone added |
| 382 | 60 | 2 days | 11 | .01 mole resorcinol added |
| 374 | 98 | 9 days | 11 | .014 mole diphenylamine added, mean of two results |
| 431 | 96 | 9 days | 16 | .011 mole phenyl-β-naphthylamine added |
| 435 | 93 | 9 days | 11 | .012 mole dimethylaniline added |
| 373 | 100 | 16 hours | 89 | .02 mole KCN added |
| 439 | 100 | 20 hours | 89 | .025 mole $NH_4Br$ added |
| 441 | 100 | 21 hours | 89 | .014 mole diphenyl ether added |

[a] Except as otherwise noted, in these runs the solutions of hydrogen bromide in allyl bromide were sealed off in bomb tubes containing air at −75°, without any drying or distillation. (V) indicates that the reaction mixtures were dried and distilled and that then air was admitted as described in the experimental part. 1.5 moles of hydrogen bromide was used in all runs.

[b] See corresponding note to Table I.

A simple adaptation of the thiocyanate test showed that various samples of allyl bromide differed widely in their ability to oxidize ferrous ion. Colors ranging all the way from the faintest pink to a deep red were developed in the thiocyanate solution. Furthermore, our experience with additions *in vacuo* indicated that the amount of 1,3-dibromopropane formed was within wide limits roughly proportional to the oxidizing power of the allyl bromide. We have assumed that this oxidizing power is due to the "peroxide content" of the allyl bromide, although we have not isolated as yet in pure form any such compound as allyl bromide peroxide. Nevertheless, we feel justified in the assumption because an addition reaction run *in vacuo* with allyl bromide of little or no oxidizing power, but where 0.02 mole of benzoyl peroxide was added to the reaction mixture (Table III) yielded exactly the same product as if allyl bromide of high oxidizing power had been employed.

TABLE III

THE EFFECT OF SOME OXIDIZING AGENTS ON THE ADDITION OF HYDROGEN BROMIDE TO ALLYL BROMIDE IN THE ABSENCE OF AIR[a]

| No | Oxidizing agent | Mole of ox. agent | Yield, % | Reaction time | % 1,3-[b] | Remarks |
|---|---|---|---|---|---|---|
| 335 | Benzoyl peroxide | 0.023 | 95 | 18 hours | 82 | |
| 364 | Bromine | .004 | 79 | 9 days | 24 | Mean of two results |
| 366 | Lead dioxide | .005 | 26 | 18 hours | 15 | |

[a,b] See corresponding notes to Table I.

Allyl bromide is quite sensitive to oxidation by atmospheric oxygen. The pure substance has been found to give a very strong peroxide test after standing in the dark at room temperature for two months. Furthermore, while a sample of peroxide-free allyl bromide gives over 80% of 1,2-dibromopropane *in vacuo*, the same sample under identical experimental conditions will give over 70% of the 1,3 isomer if oxygen is bubbled through it for ten minutes before the addition of the hydrogen bromide (Table I, No. 363). It can also be demonstrated that the oxidizing power of the sample was increased by the ten-minute treatment with oxygen. *In our opinion, therefore, unless conditions are attained which eliminate this oxygen or peroxide effect, no statement as to the direction of addition of hydrogen bromide to a sample of allyl bromide, the peroxide content of which is unknown, is of significance.*

Clearly two alternative methods present themselves for obtaining consistently only one product in the addition of hydrogen bromide to allyl bromide. The first is to attain conditions where all the samples of allyl bromide react as if they contained large quantities of peroxide; the second is to attain conditions where all samples of allyl bromide react as if they contained no peroxides at all. Since allyl bromide is very sensitive to oxidation, the first condition is easily attained by running the reaction in the presence of air. That this air effect is due to oxygen and not to the presence of some other gas besides hydrogen bromide is shown by the fact that when the reaction is run in the presence of an inert gas such as hydrogen, nitrogen, nitric oxide or nitrogen dioxide (Table IV), the result is exactly the same for any particular sample as if the run had been made *in vacuo.*

TABLE IV

THE EFFECT OF FOREIGN GASES OTHER THAN OXYGEN ON THE ADDITION OF HYDROGEN BROMIDE TO ALLYL BROMIDE

All of these runs were prepared according to the usual vacuum drying and distillation technique. Gases were then admitted through a long tube containing phosphorus pentoxide, as shown in Fig. 3. 1.50 moles of hydrogen bromide was used in all expts.

| No. | Yield, % | Reaction, time | % 1,3[b] | Remarks |
|---|---|---|---|---|
| | | | | Commercial electrolytic hydrogen admitted |
| 250 | 90 | 8 days | 49 | No special treatment of hydrogen |
| 286 | 100 | 9 days | 83 | Hydrogen passed through alkaline potassium permanganate, concd. sulfuric acid, and silica gel |
| 291 | 98 | 9 days | 50 | |
| 292 | 100 | 9 days | 84 | |
| 302 | 84 | 10 days | 26 | Same treatment, with tower of alkaline sodium hydrosulfite added to train |
| 303 | 86 | 10 days | 40 | |
| 429 | 77 | 10 days | 20 | Hydrogen passed through tube of hot copper prepared by reduction of granulated copper oxide |
| | | | | Commercial nitrogen admitted |
| 287 | 83 | 9 days | 26 | No special treatment of nitrogen |
| | | | | Nitric oxide from sodium nitrite and acid ferrous sulfate solutions admitted |
| 372 | 92 | 9 days | 11 | Nitrogen passed through allyl bromide for 12 min. before solution of hydrogen bromide. 0.01 mole of hydroquinone present with $P_2O_5$ during drying |
| | | | | Nitrogen dioxide from copper and concentrated nitric acid admitted |
| 392 | 94 | 7 days | 17 | No special treatment of oxide |

[b] See corresponding note to Table I.

The second condition is attained with almost equal ease by the addition of an antioxidant to the reaction mixture. A wide variety of antioxidants have been used, some neutral, some basic, and some acidic. All of them affect the course of the reaction in an almost identical manner. If the antioxidant is present in sufficient quantity, the addition product, irrespective of the peroxide content of the allyl bromide or the presence or absence of oxygen, is almost entirely 1,2-dibromopropane (Tables I and II).

An explanation is perhaps due here as to our use of the word "antioxidant." That oxygen is responsible for the formation of 1,3-dibromopropane in the dark has been amply demonstrated by many experiments. Whether the materials which we call antioxidants act in the capacity of merely breaking a chain reaction, or by inactivating the double bond and decreasing the oxygen effect, or whether they effectively decompose peroxides under the experimental conditions, or remove oxygen is difficult to state on the basis of available information. We are rather inclined, from a consideration of Table V, to believe that the materials actually remove or decompose the peroxides in the allyl bromide, but only under the experimental conditions of the addition of hydrogen bromide.

TABLE V

THE PEROXIDE CONTENTS OF ALLYL BROMIDE, ALLYL ALCOHOL AND LIGROIN

These tests were carried out in the usual way by shaking the sample with 10% ammonium thiocyanate solution and crystals of ferrous ammonium sulfate. The results are expressed in the following manner. The instant intense coloration obtained with the old samples of allyl bromide and alcohol is assigned the value 4. The exceedingly faint color of the blank is considered to be 0. Intermediate values represent intermediate color intensities.

| Material tested | No. | Treatment of material | Peroxide test |
|---|---|---|---|
| Freshly prepared allyl bromide | 1 | None | 0 |
| | 2 | Oxygen passed through sample for five minutes in diffused light | 1 |
| Allyl bromide prepared two months previously | 3 | None | 4 |
| | 4 | Stood with diphenylamine a few hours at room temperature | 4 |
| | 5 | Distilled | 2 |
| | 6 | Distilled from diphenylamine | 2 |
| | 7 | 4.0 g. allyl bromide, 1.0 g. hydrogen bromide, and 0.1 g. diphenylamine stood in dark in bomb tube for nineteen hours, decanted material | 0 |
| | 8 | Same, distilled material | 0 |
| Eastman allyl alcohol, received a few months previously | 9 | None | 4 |
| | 10 | Distilled | 1 |
| | 11 | Stood with diphenylamine a few hours at room temperature | 4 |
| Ligroin, washed with concd. sulfuric acid a few months previously, and distilled, b. p. 32–35° | 12 | None | 1 |

Many materials were tried as antioxidants. Naturally the common ones such as diphenylamine, phenyl-$\beta$-naphthylamine, hydroquinone, mercaptobenzothiazole, thiophenol and thiocresol were tried and found to be effective,[8] as well as some weaker ones such as resorcinol and dimethylaniline. On the other hand, potassium cyanide, ammonium bromide, and diphenyl ether were without effect on the addition in the presence of oxygen. This indicates that the mere presence of an ammonia nitrogen atom is not the important factor, but the presence rather of a system

---

(8) The addition proceeds with approximately the same velocity in the presence of most antioxidants although the velocity is slightly higher (with and without solvents) with diphenylamine than with hydroquinone. The presence of a little tertiary butyl isocyanide, however, increases the velocity of the normal addition three- or four-fold.

which under the conditions of the experiment may selectively take away the oxygen from peroxides.

It must be borne in mind, however, that since the antioxidants mentioned above as well as glacial acetic acid and ferric and aluminum chlorides all lead to the same final result, namely, the formation of 1,2-dibromopropane even in the presence of peroxides, it is highly probable that the mechanism of their effect may differ widely from case to case.

During an experience covering about 500 additions, we have (with certain minor exceptions which will be duly noted in their places) never observed any difference between the behavior of a reaction mixture freed beforehand from peroxides and run *in vacuo*, and that of one run *in vacuo* or in air in the presence of a good antioxidant. In describing the effect of temperature, solvent, light, etc., on the addition reaction, we shall therefore refer to runs made under "peroxide-free" conditions without specifying necessarily in each case by which of the two methods just mentioned those conditions were attained.

For the proper appreciation of the entire subject matter, the reader should note that the following factors were evaluated and shown to be without effect: the addition products, 1,2- and 1,3-dibromopropanes (Table VI); phosphorus pentoxide and phosphoric acid (Table VI); traces of water when the reaction mixture was not dried (Tables I and II); drying agents, the time of drying, and the concentration of hydrogen bromide (Table I); and surface catalysts (Table XVII, to be discussed later).

TABLE VI

THE ADDITION OF HYDROGEN BROMIDE TO ALLYL BROMIDE IN THE PRESENCE OF THE ADDITION PRODUCTS, PHOSPHORUS PENTOXIDE AND PHOSPHORIC ACID

| No. | Material added | Moles | Air[a] | Yield, % | Reaction, time | % 1,3[b] | Remarks |
|---|---|---|---|---|---|---|---|
| 73 | 1,2-Dibromopropane | 0.12 | Present | 94 | 3 days | 86 | |
| 74 | 1,3-Dibromopropane | .12 | Present | 87 | 3 days | 86 | |
| 235 | 1,2-Dibromopropane | 1.0 | Absent | 94 | 12 days | 36 | 2.5 moles HBr used |
| 248 | 1,3-Dibromopropane | 1.0 | Absent | 99 | 12 days | 21 | |
| 168 | Phosphoric acid | 0.01 | Present | 100 | 46 hours | 91 | |
| 175 | Phosphorus pentoxide | .1 | Present | 96 | 16 hours | 90 | |
| 174 | Phosphorus pentoxide | .1 | Present | 96 | 5 minutes | 92 | Run 20 cm. from 500-watt lamp |
| 192 | Phosphorus pentoxide | .05 | Absent | 46 | 42 hours | <30 | |
| 199 | Phosphorus pentoxide | .17 | Absent | 27 | 16 hours | <30 | |
| 220 | Phosphoric acid | .12 | Absent | 30 | 20 hours | 10 | |

[a] Except where noted otherwise, 1.5 moles of hydrogen bromide was used. When air was present, the bomb tubes were sealed off without evacuation, and without drying or distillation of the reaction mixture. Nos. 174 and 175 were shaken for an hour at −75° before they were allowed to warm to room temperature. When air was absent, the reaction mixtures were dried and distilled *in vacuo* into another bomb tube. This latter tube contained phosphoric acid or phosphorus pentoxide when these substances were present. [b] See corresponding note to Table I.

**2. The Temperature Effect.**[9]—Our experiments on the effect of changes of temperature on the addition of hydrogen bromide to allyl bromide were conducted at temperatures ranging from −75 to 100°. Some of these results are given in Table VII and they are summarized graphically in Fig. 1. Within the limits investigated by us the effect of increase of temperature is to increase the velocity of both the normal 1,2 addition and the peroxide-catalyzed 1,3 addition. The latter addition, however, has a temperature coefficient 1.5–2 times that of the former.

TABLE VII

THE EFFECT OF TEMPERATURE ON THE ADDITION OF HYDROGEN BROMIDE TO ALLYL BROMIDE IN THE ABSENCE OF SOLVENTS

| No. | Temp., °C. | Yield, % | Reaction time | % 1,3-[b] | Remarks |
|---|---|---|---|---|---|
| Air present. 1.5 moles of hydrogen bromide used. Reaction mixture sealed off with air at −75° without drying | | | | | |
| 427 | −75 | 73 | 1 hour | 95 | Old allyl bromide reacted during solution of hydrogen bromide |
| 66 | 0 | 62 | 10 days | 16 | |
| 67 | 0 | 65 | 10 days | 25 | |
| 123 | 0 | 72 | 21 days | 46 | |
| 112 | 0 | 100 | 48 hours | 92 | |
| 396 | 0 | 100 | 6 days | 80 | Reaction mixture dried and distilled. Dried air admitted |
| 121 | 7 | 64 | 11 days | 18 | |
| 101 | 9 | 90 | 15 days | 71 | |
| 122 | 14 | 100 | 10 days | 95 | |
| 102 | 16 | 87 | 9 days | 65 | |
| 124 | 20 | 100 | 6 days | 90 | |
| 125 | 28 | 100 | 3 days | 93 | |
| 127 | 37 | 100 | 3 days | 84 | |
| Air absent. 1.5 moles of hydrogen bromide used. Reaction mixture dried and distilled, run *in vacuo* | | | | | |
| 132 | 0 | 81 | 50 days | 13 | Mean of two results |
| 133 | 14 | 72 | 18 days | 8 | |
| 131 | 29 | 71 | 6 days | 17 | Mean of two results |
| 134 | 37 | 92 | 6 days | 43 | Mean of three results |
| 190 | 56 | 99 | 23 hours | 90 | Mean of three results |
| 289 | 56 | 78 | 13 hours | 63 | |
| 309 | 56 | 75 | 20 hours | 50 | |
| 314 | 56 | 91 | 28 hours | 68 | |
| 146 | 76 | 99 | 12 hours | 88 | Mean of three results |
| 319 | 76 | 99 | 18 hours | 82 | Dried overnight with a very large quantity of $P_2O_5$ |
| 158 | 100 | 100 | 24 hours | 89 | Mean of two results |
| 376 | 76 | 75 | 13 hours | 26 | 0.011 mole hydroquinone present |
| 383 | 76 | 86 | 13 hours | 16 | .011 mole resorcinol present |
| 416 | 76 | 99 | 16 hours | 16 | .014 mole diphenylamine present. Mean of two results |
| 390 | 100 | 89 | 13 hours | 33 | .011 mole hydroquinone present |
| 434 | 100 | 100 | 16 hours | 18 | .014 mole diphenylamine present |

[b] See corresponding note to Table I.

---

[9] All of the experiments of which the results are reported in this section were made in the dark in the absence of solvents.

So marked is the difference that at low temperatures, large amounts of 1,2-dibromopropane are formed even in the presence of air, if the initial peroxide content of the allyl bromide is low. Otherwise, the 1,3-dibromide is formed (Note No. 427). On the other hand, at high temperatures the formation of 1,3-dibromopropane is so rapid that the merest traces of peroxide, even when air is carefully removed, are sufficient to cause the formation of this product.

This explanation accounts for certain small discrepancies between the results obtained at high temperatures. At such temperatures, where the 1,3 addition catalyzed by peroxides is greatly accelerated, even the slightest traces of peroxides affect the course of the reaction and cause the formation of a greater amount of the 1,3-dibromide than would have been formed had the reaction been carried out at a lower temperature.

For this reason, if at a high temperature peroxides are present and an antioxidant is to be used, the latter must be extremely effective if all peroxide effect is to be eliminated. We have noted considerable variation in this respect among the antioxidants which we have employed. However, if the antioxidant used is one of the best the amount of 1,3-dibromopropane formed is, within the limits of error, the same as that obtained at low temperatures. *In vacuo* and under so-called "peroxide-free conditions," but in the absence of an antioxidant, we have not obtained such clear-cut results. It is extremely difficult under the conditions of the experiment without an effective antioxidant to eliminate all traces of peroxides, and so reactions run under the conditions just described uniformly yield more 1,3-dibromopropane with increasing temperature.

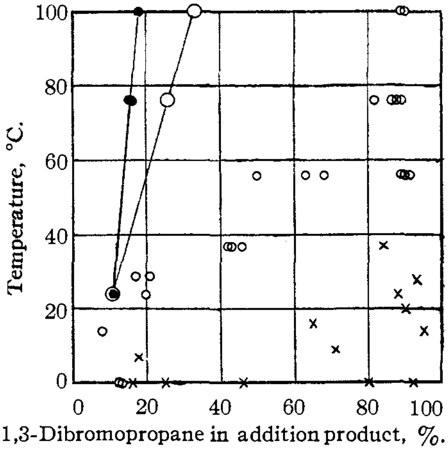


Fig. 1.—The effect of temperature on the addition of hydrogen bromide to allyl bromide, a summary of Table VII except that results for 24° are condensed from Tables I and II. X represents results obtained in the presence of air; small open circles, in the absence of air; large open circles, in the absence of air and the presence of hydroquinone; and small solid circles, in the absence of air and the presence of diphenylamine.

It is easy to see that under these circumstances workers whose attention has not been called to the effect of the peroxide in directing the addition might interpret the increase in yield of 1,3-dibromopropane with increasing temperature as a primary temperature effect. *In fact, it has been stated that high temperature favors the formation of the 1,3-, and low tempera-*

*ture the 1,2-dibromide. This statement is true (as our own data testify) but not exactly in the sense intended.* That the temperature effect is subsidiary to the peroxide effect is clearly shown by the runs made in the presence of antioxidants where a large increase in temperature causes scarcely any change in the composition of the addition product. In the absence of such antioxidants, heat favors the formation of 1,3-dibromopropane because peroxides are more effective in causing formation of this product at high temperatures than they are at low temperatures.

**3. The Solvent Effect.**—In view of what has already been said about the effect of peroxides on the addition of hydrogen bromide to allyl bromide, it was necessary to take this factor into account in the study of the effect of solvents.

The first important fact to be noted from our work with various solvents is that in the dark under "peroxide-free conditions" (presence of antioxidants) all the solvents used were without effect on the direction of addition, *i. e.*, the product was always about 90% 1,2-dibromopropane: (water, Table IX; acids, Table X; aqueous acetic acid, Table XI; ligroin, chloroform, carbon tetrachloride, carbon disulfide, Table XII; acid halides, Table XIII). In particular, the dielectric constant of the solvent made no detectable difference in the composition of the addition product under peroxide-free conditions, although this constant varied from 1.83 in the case of ligroin (pentane) to 80.0 in the case of water (Table VIII). That the dielectric constant may have an effect upon the velocity of addition is self-

TABLE VIII

THE CORRELATION BETWEEN THE DIELECTRIC CONSTANT OF THE SOLVENT AND THE DIRECTION OF ADDITION OF HYDROGEN BROMIDE TO ALLYL BROMIDE

The results listed in this table represent what we believe to be the best values from Tables VI, IX, X, XII and XIII. The dielectric constants of the pure solvents are for a temperature of 20°.

| Solvent | Dielectric constant | % 1.3 (remainder of product is 1,2) | | |
|---|---|---|---|---|
| | | Air present | Air absent | |
| | | | Antioxidant Absent | Antioxidant Present |
| Pentane (ligroin) | 1.83 | | 90 | 11 |
| Carbon tetrachloride | 2.24 | | 54 | 12 |
| Carbon disulfide | 2.6 | 95 | 14 | |
| Propionic acid | 3.19 | | 13 | |
| 1,2-Dibromopropane | 4.35 | 86 | 36 | |
| Chloroform | 5.05 | 87 | 42 | 12 |
| Acetic acid | 6.4 | 16 | 12 | |
| Acetyl bromide | 16.5 | 25 | 15 | |
| Benzoyl bromide | 19.0 | 20 | | |
| Formic acid | 47.9 | | 11 | |
| Water | 80.0 | 85 | 16 | 11 |
| 1,3-Dibromopropane | | 86 | 21 | |
| β-Phenylpropionic acid | | 11 | | |
| Hydrogen bromide | 3.82 | | | |
| Allyl bromide | 7.0 | 89 | 15 | 11 |

TABLE IX

THE ADDITION OF HYDROGEN BROMIDE TO ALLYL BROMIDE IN THE PRESENCE OF WATER

| No. | Moles HBr | Moles $H_2O$ | %[c] HBr | Air[d] | Yield, % | Reaction time | % 1.3-[e] | Remarks |
|---|---|---|---|---|---|---|---|---|
| Runs in which less than 1% of water was present | | | | | | | | |
| Run at 0° | | | | | | | | |
| 114 | 1.51 | 0.03[a] | | Present | 91 | 48 hours | 95 | |
| 395 | 1.51 | .13 | | Present | 100 | 4 days | 84 | |
| 430 | 1.50 | .05 | | Present | 97 | 22 days | 29 | |
| Run at room temperature | | | | | | | | |
| 126 | 1.50 | .03[a] | | Present | 100 | 3 days | 96 | (28°) |
| 337 | 1.53 | .02[b] | | Present | 97 | 17 hours | 87 | |
| 330 | 1.53 | .02[b] | | Absent (1) | 32 | 21 hours | 18 | |
| 336 | 1.50 | .02[b] | | Absent (1) | 100 | 10 days | 63 | |
| 351 | 1.56 | .03[a] | | Absent (1) | 81 | 7 days | 21 | |
| 218 | 1.53 | .054 | | Absent (2) | 100 | 19 hours | 84 | |
| 399 | 1.50 | .055 | | Absent (1) | 98 | 7 days | 8 | 0.014 mole diphenylamine present |
| Run at 76° | | | | | | | | |
| 343 | 1.50 | .03[a] | | Absent (1) | 98 | 9 hours | 90 | |
| 418 | 1.50 | .054 | | Absent (1) | 99 | 16 hours | 18 | 0.014 mole diphenylamine present |
| Runs in which more than 5% of water was present | | | | | | | | |
| Run at room temperature | | | | | | | | |
| 358 | 2.54 | 1.98 | 85.2 | Present | 100 | 40 hours | 83 | Mean of two results |
| 357 | 2.52 | 1.98 | 85.2 | Absent (1) | 100 | 41 hours | 83 | Mean of three results |
| 327 | 2.26 | 1.51 | 87.1 | Absent (2) | 99 | 4 days | 16 | |
| 400 | 2.52 | 1.97 | 85.0 | Absent (1) | 89 | 4 days | 11 | 0.014 mole diphenylamine present |
| Run at 76° | | | | | | | | |
| 342 | 2.55 | 1.90 | 85.8 | Absent (1) | 81 | 9 hours | 61 | |
| 384 | 2.55 | 2.01 | 85.0 | Absent (2) | 100 | 13 hours | 76 | |
| 417 | 2.55 | 2.00 | 85.0 | Absent (1) | 100 | 16 hours | 21 | 0.014 mole diphenylamine present |
| Run at 100° | | | | | | | | |
| 298 | 1.98 | 2.02 | 81.5 | Absent (2) | 100 | 16 hours | 87 | |
| Runs in which about 50% of water was present | | | | | | | | |
| Run at room temperature | | | | | | | | |
| F3 | 2.78 | 18.8 | 40.0 | Present | <2 | 108 days | .. | |
| F4 | 5.00 | 33.6 | 40.0 | Present | <5 | 40 days | .. | Run 60 cm. from 100-watt lamp |
| Run at about 125° | | | | | | | | |
| 290 | 3.93 | 26.4 | 40.0 | Present | <10 | 11 hours | .. | Only tar obtained |

[a] Estimated. Allyl bromide saturated with water at room temperature before addition of hydrogen bromide. [b] Same as [a] but saturated at 0°. [c] Ratio of weight of hydrogen bromide to weight of hydrogen bromide plus water. [d] When air was present, the bomb tubes were sealed off with air at −75°. When air was absent, it was removed (1) by evacuation of the bomb tube without distillation or (2) by evacuation and subsequent vacuum distillation. [e] See note [b] to Table I.

TABLE X

THE ADDITION OF HYDROGEN BROMIDE TO ALLYL BROMIDE IN GLACIAL ACETIC ACID (INCLUDING ALSO A FEW RUNS IN OTHER ACIDS)

| No. | Moles HBr | Moles acid | Air[a] | Yield, % | Reaction time | % 1,3-[b] | Remarks |
|---|---|---|---|---|---|---|---|
| Run in the dark at room temperature | | | | | | | |
| Acetic acid | | | | | | | |
| F1 | 1.87 | 8.88 | Present | <5 | 22 hours | .. | |
| X1 | 3.73 | 15.8 | Present | >60 | 7 days | 5 | |
| X3 | 2.80 | 6.59 | Present | 89 | 15 days | 8 | |
| X6 | 2.64 | 4.55 | Present | 96 | 13 days | 5 | |
| 280 | 2.51 | 1.50 | Present | 100 | 4 days | 19 | |
| 406 | 2.50 | 1.50 | See remark | 100 | 45 hours | 16 | Bomb tube filled with oxygen |
| 352 | 2.50 | 1.50 | Absent | 99 | 42 hours | 12 | |
| Other acids | | | | | | | |
| 34 | 1.50 | 1.50 | Present | 92 | 7 days | 11 | β-Phenylpropionic acid |
| 297 | 2.66 | 1.50 | Absent | 100 | 7 days | 13 | Propionic acid |
| 325 | 2.49 | 1.50 | Absent | 96 | 43 hours | 10 | Formic acid[c] |
| 414 | 2.43 | 1.50 | Absent | 76 | 15 hours | 12 | Formic acid, mixture flushed with $N_2$ before solution of HBr |
| Acetic acid | | | | | | | |
| Run at 76° | | | | | | | |
| 197 | 1.50 | 1.49 | Present | 99 | 17 hours | 17 | |
| Run near 100-watt[d] lamp at room temperature | | | | | | | |
| X2 | 4.0 | 8.0 | Present | 85 | 66 hours | 10 | 15 cm. from lamp, mean of three results |
| X11 | 1.50 | 0.33 | Present | 100 | 5 days | 40 | 15 cm. from lamp |
| Run near 500-watt[d] lamp at room temperature | | | | | | | |
| 179 | 1.51 | 1.50 | Present | 9 | 30 min. | Mostly 1,2- | 15 cm. from lamp |
| 186 | 2.3 | 1.50 | Present | 98 | 15 hours | 26 | 20 cm. from lamp |
| 345 | 2.58 | 1.50 | Absent | 100 | 14 hours | 24 | 15 cm. from lamp |
| 413 | 2.66 | 1.50 | Absent | 99 | 15 hours | 17 | 15 cm. from lamp, 0.011 mole quinone present, mixture flushed with nitrogen before solution of hydrogen bromide |
| Run near 500-watt[d] lamp at temperature of 4–7° | | | | | | | |
| 266 | 2.66 | 1.50 | Present | 95 | 16 hours | 42 | 20 cm. from lamp, mean of two results |
| 349 | 2.50 | 1.50 | Absent | 76 | 8 hours | 49 | 12 cm. from lamp |
| 436 | 2.50 | 1.50 | See remark | 98 | 15 hours | 75 | 7.5 cm. from lamp, allyl bromide and acetic acid flushed with, and bomb tube filled with, oxygen |
| 437 | 2.50 | 1.50 | Absent | 92 | 15 hours | 70 | 7.5 cm. from lamp, 0.014 mole of diphenylamine present, allyl bromide and acetic acid flushed separately with $N_2$ |

---

[a] When air was present, the bomb tubes were sealed off with air at −75°, without drying of the reaction mixture. Except for No. 437, air was removed from the runs with

acetic acid by simply evacuating the bomb tubes. In the runs with other acids, and No. 437 with acetic acid, the hydrogen bromide and allyl bromide were dried and distilled *in vacuo* into the solvent.

[b] See corresponding note to Table I.

[c] Under the experimental conditions, formic acid was largely decomposed into water and carbon monoxide. Special precautions were taken in handling and opening the bomb tubes because of the large pressures developed.

[d] The 100-watt lamp was an ordinary frosted one. The 500-watt lamp was an incandescent projection lamp.

TABLE XI

THE ADDITION OF HYDROGEN BROMIDE TO ALLYL BROMIDE IN AQUEOUS ACETIC ACID SOLUTION

| No. | Moles HBr | Moles acetic acid | $\frac{\text{Wt. AcOH}}{\text{wt. (AcOH + H}_2\text{O)}}$ % | Air[a] | Yield, % | Reaction, time | % 1,3-[b] | Remarks |
|---|---|---|---|---|---|---|---|---|
| | | | | Run in the dark at room temperature | | | | |
| 276 | 2.52 | 1.50 | 97.7 | Present | 100 | 4 days | 28 | |
| 237 | 1.53 | 1.50 | 97.0 | Present | 93 | 73 hours | 46 | |
| 236 | 1.81 | 1.50 | 93.9 | Present | 98 | 73 hours | 71 | |
| 356 | 2.50 | 1.50 | 90.0 | Present | 100 | 40 hours | 64 | |
| 140 | 1.54 | 1.53 | 90.0 | Present | 96 | 9 days | 82 | |
| 408 | 2.54 | 1.20 | 75.0 | Present | 100 | 42 hours | 82 | |
| 409 | 2.52 | 1.20 | 75.0 | Present | 90 | 45 hours | 18 | 0.011 mole hydroquinone present |
| 338 | 2.55 | 1.51 | 90.3 | Absent | 100 | 5 days | 24 | |
| 355 | 2.54 | 1.50 | 90.0 | Absent | 95 | 41 hours | 15 | Allyl bromide and acetic acid flushed with $N_2$ before solution of HBr |
| 360 | 2.50 | 1.50 | 79.0 | Absent | 92 | 43 hours | 26 | |
| 410 | 2.61 | 1.20 | 75.0 | Absent | 100 | 42 hours | 33 | |
| | | | | Run near 500-watt lamp[d] at room temperature | | | | |
| 255 | 1.68 | 1.50 | 97.8 | Present | 97 | 16 hours | 50 | 13 cm. from lamp |
| 275 | 2.50 | 1.50 | 97.8 | Present | 100 | 16 hours | 38 | 15 cm. from lamp |
| 348 | 2.55 | 1.50 | 90.2 | Absent | 100 | 14 hours | 63 | 15 cm. from lamp |

[a] When air was present, the bomb tubes were sealed off with air at −75° without special treatment of the reaction mixture. Otherwise, the bomb tubes were simply evacuated. [b,d] See corresponding notes to Tables I and X, respectively.

evident. However, in addition to this notion, many chemists consider also the position taken by the addenda to be influenced by the solvent.[9a] The reference to the list of authors is not at all indicative of the extent to which this notion is prevalent. There are many more scattered allusions to that effect in the literature and the notion had been widely accepted by the chemists with whom the authors discussed this problem prior to the completion of their work.

Indeed, Table VIII shows that if no attention is paid to the peroxide content of the allyl bromide and the "antioxidant" effect of the solvent used, it is easy to obtain results of a highly deceptive nature. For instance, a series of additions made in the presence of air, with solvents of high di-

---

(9a) Michael and Zeidler, *Ann.*, **385**, 265 (1911); Ipatiev and Ogonowski, *Ber.*, **36**, 1988 (1903).

### TABLE XII

### THE ADDITION OF HYDROGEN BROMIDE TO ALLYL BROMIDE IN THE PRESENCE OF LOW-BOILING PARAFFIN HYDROCARBONS, CHLOROFORM, CARBON TETRACHLORIDE, AND CARBON DISULFIDE

Except as noted otherwise, the runs listed in this table were dried, distilled *in vacuo*, and sealed off without the entrance of air, as described in the experimental part, and the additions took place in the dark at room temperature. 1.5 moles of solvent were used.

| No. | Moles HBr | Solvent | Yield,[a] % | Reaction time | % 1,3-[b] | Remarks |
|---|---|---|---|---|---|---|
| A1 | 1.50 | Heptane | 70 | 6 days | 92 | Run 20 cm. from 100-watt[d] lamp. Sealed off with air without drying or distillation |
| 257 | 2.55 | Chloroform | 72 | 9 days | 92 | Undried air admitted |
| 72 | 1.54 | Carbon disulfide | 84 | 6 days | 95 | Sealed off with air without drying or distillation |
| 147 | 2.25 | Ligroin (1)[c] | 68 | 13 days | 90 | Mean of three results |
| 316 | 2.25 | Ligroin (2) | 75 | 15 days | 90 | |
| 202 | 2.45 | Ligroin (1) | 79 | 35 days | 92 | Mean of two results. Run at 0° |
| 247 | 1.79 | Ligroin (1) | 39 | 25 days | 90 | Run at 0° |
| 329 | 2.50 | Ligroin (3) | 87 | 48 hours | 7 | 0.02 mole anh. $FeCl_3$ added (*cf.* Table XVI) |
| 269 | 2.67 | Chloroform | 90 | 9 days | 88 | Mean of two results |
| 306 | 2.52 | Chloroform | 73 | 14 days | 42 | |
| 318 | 2.52 | Chloroform | 89 | 16 days | 89 | Dried overnight with large excess of $P_2O_5$ |
| 304 | 2.55 | Chloroform | 57 | 28 days | 33 | Run at 0° |
| 183 | 2.04 | Carbon tetrachloride | 72 | 13 days | 83 | |
| 293 | 2.64 | Carbon tetrachloride | 66 | 9 days | 67 | |
| 305 | 2.56 | Carbon tetrachloride | 48 | 10 days | 54 | |
| 315 | 2.56 | Carbon tetrachloride | 77 | 15 days | 77 | Dried overnight with large excess of $P_2O_5$ |
| 307 | 2.50 | Carbon tetrachloride | 28 | 31 days | 7 | Run at 0° |
| 148 | 2.60 | Carbon disulfide | 53 | 13 days | 14 | Mean of two results |
| 187 | 2.50 | Carbon disulfide | 91 | 14 hours | 95 | Mean of three results. Run 15 cm. from 500-watt[d] lamp |
| 371 | 2.55 | Ligroin (3) | 18 | 13 days | 20 | 0.011 mole hydroquinone |
| 397 | 2.50 | Ligroin (3) | 38 | 26 days | 11 | 0.011 mole hydroquinone |
| 401 | 2.50 | Carbon tetrachloride | 59 | 26 days | 12 | 0.011 mole hydroquinone |
| 402 | 2.50 | Chloroform | 78 | 26 days | 12 | 0.011 mole hydroquinone |
| 403 | 2.50 | Ligroin (3) | 57 | 26 days | 11 | 0.014 mole diphenylamine |
| 404 | 2.55 | Carbon tetrachloride | 74 | 26 days | 12 | 0.014 mole diphenylamine |
| 405 | 2.50 | Chloroform | 81 | 26 days | 12 | 0.014 mole diphenylamine |

[a] The yields in this table represent the weight of dibromopropanes recovered after removal of the solvent and allyl bromide by fractional distillation. Because of comparatively large losses in working with very small quantities of material 10% or more should be added to these values to make them comparable with the yields as given in other tables.

[b,d] See corresponding notes in Tables I and X, respectively.

[c] Commercial petroleum ether was washed several times with concentrated sulfuric acid and then with water, dried, and fractionally distilled. From various lots, different fractions were collected which are noted in the table by numerals: (1) 30–41°, (2) 41–60° and (3) 32–35°. For purposes of calculation, the ligroin is assumed to be pentane.

electric constant and some ability to act as antioxidants on the one hand, and with solvents of low dielectric constant and no ability to act as antioxidants on the other, might easily suggest that high dielectric constants favored the formation of the 1,2-, and low the formation of the 1,3-dibromide. However, as soon as we introduce the use of antioxidants as an extreme precaution, the apparently consistent series has no foundation. Thus, of about a dozen different solvents of widely varying properties that were tried, none affected perceptibly the order of addition when the effect of oxygen was removed, although the rate of addition with these solvents may have varied by a factor of one hundred or more. We are thus forced to the conclusion that the dielectric constant of the solvent has no direct effect on the direction of addition but that the solvent may affect the stability of peroxides, resist the effect of oxygen, or affect the relative velocities of the two competing reactions. The resistance of some solvents to the oxygen effect may be due to any or all of three causes: first, the stability of the peroxides of allyl bromide may vary with the solvent (note particularly the striking diminution of the antioxidant effect of acetic acid upon dilution with water, Table XI, and how it may be restored by the addition of an antioxidant); second, the peroxide content of the solvent itself may vary (Table V, note also the effect of small quantities of benzoyl peroxide, Table III); and third, the variation due to the wide differences in the velocities of addition to give 1,2-dibromopropane, *i. e.*, the velocity of the normal addition may be more affected by the solvent than that of the peroxide-catalyzed addition.

It is interesting to note here that apparently the dielectric constant of the solvent has considerable influence on the velocity of addition, yet there is no simple direct relationship. One might say from a superficial examination of the accumulated facts that the higher the dielectric constant of the solvent, the greater will be the velocity of addition. Nevertheless, careful examination shows that while the statement is confirmed by the runs with antioxidants with ligroin, carbon tetrachloride, and chloroform in Table XII (the yield in twenty-eight days follows exactly the order of increasing dielectric constant), and is also true in comparing formic and acetic acids, it does not hold when different types of solvents are compared. Thus, both allyl bromide and acetyl bromide have higher dielectric constants than acetic acid, but the addition in the latter solvent is far faster than in the absence of a solvent or in the presence of acetyl bromide. Another set of results which are difficult to explain solely on the basis of dielectric constants are those with water (Table IX). Considering only the runs in which the principal product was 1,2-dibromopropane, it may be seen that the addition of a little water (85% aqueous hydrogen bromide) accelerates the addition, but in 40% aqueous hydrogen bromide, practically no addition takes place.

TABLE XIII

THE ADDITION OF HYDROGEN BROMIDE TO ALLYL BROMIDE IN THE PRESENCE OF ACETYL BROMIDE AND BENZOYL CHLORIDE

1.5 moles of acetyl bromide was used as solvent in all of these runs excepting two, where note is made of the use of benzoyl chloride.

| No. | Moles HBr | Air[a] | Yield, % | Reaction time | % 1,3-[b] | Remarks |
|---|---|---|---|---|---|---|
| | | | Run in the dark at room temperature | | | |
| 141 | 1.70 | Present | 91 | 11 days | 25 | |
| 378 | 2.50 | Present | 99 | 12 days | 46 | |
| 260 | 2.33 | Present | [c] | 9 days | 20 | Benzoyl chloride |
| 411 | 2.50 | Absent | 96 | 14 days | 15 | |
| | | | Run at 76° | | | |
| 256 | 1.63 | Present | 92 | 16 hours | 74 | |
| 354 | 2.54 | Present | 97 | 8 hours | 55 | |
| 344 | 2.58 | Absent | 93 | 9 hours | 31 | |
| 353 | 2.57 | Absent | 94 | 9 hours | 24 | |
| | | | Run near 500-watt lamp[d] at room temperature | | | |
| 180 | 1.51 | Present | 17 | 30 min. | .. | Run 15 cm. from lamp |
| 188 | 2.14 | Present | 100 | 15 hours | 89 | Run 20 cm. from lamp |
| 265 | 2.66 | Present | 100 | 19 hours | 92 | Run 15 cm. from lamp |
| 347 | 2.56 | Absent | 100 | 14 hours | 91 | |
| 261 | 2.45 | Present | [c] | 12 hours | 92 | Run 15 cm. from lamp, benzoyl chloride |

[a] When air was present, the bomb tubes were sealed off with air at −75° without special treatment of the reaction mixture. When air was absent, it was generally removed by evacuation of the bomb tube without drying or distillation of the reaction mixture. In No. 411, nitrogen was passed through the mixture of allyl bromide and acetyl bromide before the solution of hydrogen bromide. The whole reaction mixture was then dried and distilled *in vacuo*.

[b,d] See corresponding notes to Tables I and X, respectively.

[c] Attempts were made to remove benzoyl chloride from the reaction products by washing with sodium carbonate, sodium hydroxide and concentrated sulfuric acid, but without much success. Because of the large losses of material, nothing can be stated about the yields except that they were probably good.

It is possible that the solvent may affect the association of allyl bromide, if allyl bromide can be associated. Mixtures of allyl bromide and a solvent were made up to find the relation between the mole fraction of the solvent in the mixtures and their indices of refraction. In Fig. 2 the results of these experiments with heptane, acetic acid, chloroform, 1,3-dibromopropane and carbon disulfide are plotted. With none of these substances was the index of refraction exactly a linear function of the mole fraction of allyl bromide in the mixtures. The curves for mixtures of allyl bromide and heptane or carbon disulfide lie well below the straight lines joining the indices of refraction of allyl bromide and the solvents used, but the curves for mixtures of allyl bromide with acetic acid, chloroform and 1,3-dibromopropane lie slightly above the corresponding straight lines. The deviation of the latter group of curves is small but well beyond the experimental error and may be explained by a slight contraction of volume on mixing the two liquids. The deviation of the curves for the mixtures with heptane or carbon disulfide is much larger and in the opposite direction. To explain this latter deviation by a change of volume on mixing the two liquids, we should have to assume that the mixture is of much greater volume than the sum of the individual volumes of the liquids of which the mixture is comprised. The deviation is so large that there may be some very unusual condition existing in these mixtures, such as association or compound formation.

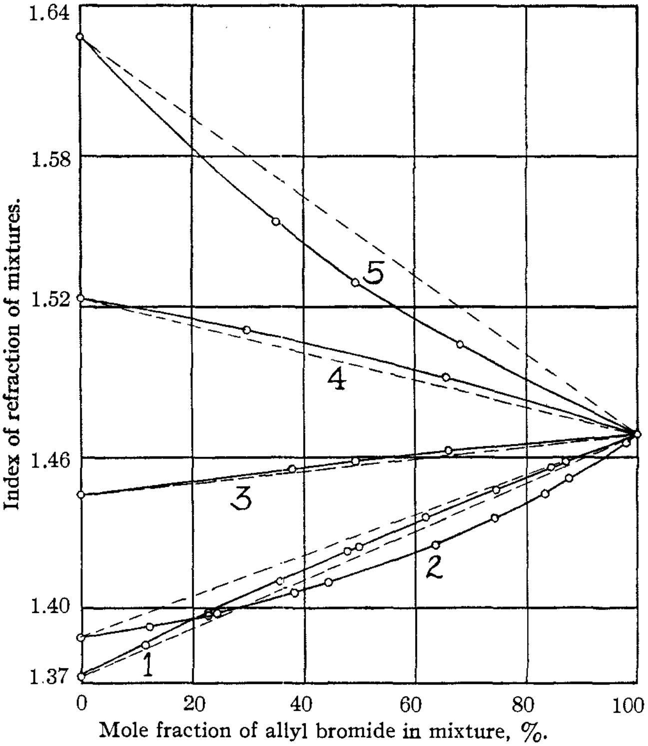


Fig. 2.—Indices of refraction of mixtures of allyl bromide with various solvents: (1) acetic acid, (2) heptane, (3) chloroform, (4) 1,3-dibromopropane, and (5) carbon disulfide. The straight broken lines are inserted to show the deviation of the curves from straight lines.

**4. The Temperature Effect in Solvents.**—Without undertaking a detailed analysis of the combined effects of solvent and temperature, it may be stated briefly that these effects are essentially independent of one another. All of the statements made about the temperature effects without a solvent and about the effect of solvents on the peroxide effect may be applied without change to reactions involving both solvents and change of temperature. We have observed no instance where the presence of a solvent seriously affected the ratio of the temperature coefficients of the two addition reactions.

The resistance of glacial acetic acid to the peroxide effect at 76°, even in the presence of air (Table X), is rather remarkable. This property of resisting the effect of peroxides seems to be common to carboxylic acids, and to a lesser extent to the acid halides (Table XIII).

**5. The Light Effect.**—The effect of light on the addition of hydrogen bromide to allyl bromide was first studied with samples of the latter which *in vacuo* and in the dark reacted in ten days to give 80–90% of a product containing about 80% 1,2-dibromopropane. Under strong illumination, the addition was sometimes complete within thirty minutes (Table XIV), and the product was about 90% 1,3-dibromopropane. Temperature lowering to 5° had no effect upon the latter reaction except to slow it down.

TABLE XIV

THE EFFECT OF LIGHT ON THE ADDITION OF HYDROGEN BROMIDE TO ALLYL BROMIDE

Except as noted otherwise, these reaction mixtures were dried and distilled as described in the experimental part. The additions took place in the absence of air at about 30°[a] and at a distance of a few centimeters from a 500-watt incandescent projection lamp. 1.5 moles of hydrogen bromide was used.

| No. | Distance from lamp, cm. | Yield, % | Reaction time | % 1,3-[b] | Remarks |
|---|---|---|---|---|---|
| 173 | 18 | 100 | 20 min. | 90 | Sealed off with air without drying or distillation Mean of two results |
| X5 | 18 | 89 | 15 days | 90 | 100-watt lamp used. Allyl bromide saturated repeatedly with HBr at −10° |
| 150 | 15 | 100 | 45 hours | 93 | Mean of four results |
| 162 | 20 | 100 | 42 hours | 95 | Dried overnight with large excess $P_2O_5$ |
| 176 | 15 | 99 | 30 min. | 92 | |
| 206 | 15 | 99 | 60 min. | 92 | Thermometer[a] in bomb tube. |
| 322 | 16 | 77 | 60 min. | 92 | Thermometer[a] in bomb tube. Mean of two results |
| 341 | 13 | 100 | 60 min. | 95 | Thermometer[a] in bomb tube. Allyl bromide saturated with water. Reaction mixture not dried or distilled. Bomb tube evacuated |
| 169 | 20 | 100 | 60 min. | 93 | Dried with $Na_2SO_4$ instead of $P_2O_5$. Mean of three results |
| 375 | 12 | 68 | 13 hours | 82 | 0.011 mole hydroquinone present |
| 391 | 12 | 94 | 14 hours | 79 | 0.014 mole diphenylamine present |
| 444 | 10 | 91 | 16 hours | 65 | 0.029 mole thiocresol present |
| 271 | 20 | 80 | 3 hours | 92 | Run at 5–10°, mean of two results |
| 446 | 6.5 | 54 | 20 hours | 39 | Run at 5–6°, 0.048 mole thiocresol present |

[a] The thermometer in No. 206 showed that a maximum temperature of 54° was reached at the end of 18 min. and that the temperature dropped slowly thereafter to reach 33° at the end of the hour. The other three runs attained maxima of about 40° in about twenty minutes. All were at a temperature of −75° when started. No. 206 showed a definite decrease in the rate of temperature rise at about 30°. However, twelve minutes after starting, the temperature began to rise suddenly and rapidly from 31°.

[b] See corresponding note to Table I.

The effect of antioxidants on the addition with full illumination will be discussed later.

Table XV shows that light of all wave lengths accelerates both reactions. In the absence of air and antioxidants, the short wave lengths have a

TABLE XV

THE EFFECT OF LIGHT FROM DIFFERENT SPECTRAL REGIONS UPON THE ADDITION OF HYDROGEN BROMIDE TO ALLYL BROMIDE

All of these reaction mixtures were dried, distilled, and run *in vacuo*.[6] A 500-watt incandescent projection lamp was used for illumination. The glass color filters used were the products of the Corning Glass Works, and their names and characteristics are taken from the Corning catalog. When one limit of transmission of a filter is omitted, it is unknown and beyond the visible region. In those runs where the yields were too poor to isolate the addition product, the product was probably 1,3-dibromopropane. The additions took place at about 30–35°, and except as noted, 1.5 moles of hydrogen bromide was used.

| No. | Color filter used | Transmission, Å. | Distance from lamp to bomb tube | Yield, % | Reaction, time | % 1.3-[b] | Remarks |
|---|---|---|---|---|---|---|---|
| 224 | Cardboard (blank) | None | 12 | 0.2 | 30 min. | .. | |
| 225 | Heat-resisting (H.R.) signal red | 6200– | 12 | 1 | 30 min. | .. | |
| 226 | H.R. medium yellow | 5500– | 12 | 2 | 30 min. | .. | |
| 229 | Dark theatre blue | 3900–5200 | 12 | 11 | 30 min. | .. | |
| 230 | Violet | –4800 | 12 | 1 | 30 min. | .. | |
| 227 | Noviol O | 3900– | 12 | 25 | 30 min. | .. | |
| 231 | Red-purple Ultra | 3200–4200 | 12 | 47 | 30 min. | .. | |
| 221 | Red-purple Ultra | also >7200 | 14 | 97 | 55 min. | 92 | |
| 240 | Noviol O | 3900– | 12 | 78 | 50 min. | 92 | |
| 239 | Noviol C | 4600– | 12 | 65 | 50 min. | 92 | |
| 438 | H.R. signal red + Noviol C | 6200– | 8 | 100 | 3 hours | 89 | |
| 213 | 39 mm. 2% aq. $CuCl_2$ soln. | 3400–7000 | 15 | 88 | 30 min. | 92 | |
| 217 | 18 mm. sat. aq. $K_2$-$Cr_2O_2$ | 5150–[10] | 15 | 100 | 4 hours | 92 | |
| | 0.014 mole of diphenylamine was also present in the following runs: | | | | | | |
| 419 | Red-purple Ultra | 3200–4200 also >7200 | 10 | 99 | 24 hours | 70 | 1.75 moles HBr |
| 420 | Noviol C | 4600– | 10 | 98 | 24 hours | 33 | 1.75 moles HBr |
| 421 | Noviol C + H.R. signal red | 6200– | 10 | 92 | 24 hours | 18 | 1.92 moles HBr |
| 424 | Red-purple Ultra + 18 mm. 2.8% $CuSO_4$ soln.[11] | 3200–4200 | 12 | 92 | 24 hours | 59 | 1.92 moles HBr |
| 432 | Red-purple Ultra + 18 mm. 2.8% $CuSO_4$ soln. | 3200–4200 | 10 | 94 | 24 hours | 74 | 1.98 moles HBr |
| 425 | 18 mm. 2.8% $CuSO_4$ soln. + Noviol C | 4600–7000 | 12 | 95 | 24 hours | 29 | 2.74 moles HBr |
| 433 | 18 mm. 2.8% $CuSO_4$ soln. + Noviol C | 4600–7000 | 10 | 95 | 24 hours | 61 | 2.01 moles HBr |

[b] See corresponding note to Table I.

---

(10) Bhagwat and Dhar, *J. Indian Chem. Soc.*, **7**, 913 (1930).

(11) "International Critical Tables," McGraw-Hill Book Co., Inc., New York, 1929, Vol. V, p. 273.

greater accelerating effect than the longer ones. All wave lengths accelerate the addition to form 1,3-dibromopropane much more than the normal addition and dibromide is therefore formed to the extent of about 90%. The runs with diphenylamine show that the effect of infra-red radiation, like that of temperature, is only to exaggerate greatly the effect of small but significant quantities of peroxides. In the presence of this antioxidant, the peroxide-catalyzed reaction is inhibited and is replaced by the slower normal addition.

Light from the visible and near ultraviolet regions favors the formation of the 1,3-dibromide so strongly that even in the presence of large amounts of good antioxidants this product is formed to the extent of 30–75% depending upon the wave length and intensity of the radiation employed. Although it seems quite certain that the effect of the longer wave lengths is only to increase the effect of peroxides, the interpretation of the effect of the shorter wave lengths is less certain and will be discussed in connection with the effect of illumination on the addition in glacial acetic acid solution.

It has been shown that the addition of hydrogen bromide to allyl bromide is reversed by light in the presence of acid halides (Table XIII), heptane and carbon disulfide (Table XII) to give about 90% of 1,3-dibromopropane just as in the absence of a solvent. The effect in acetic acid solution is more complicated and to it we shall now confine our attention.

In the addition of hydrogen bromide to allyl bromide, acetic acid behaves as a moderately strong antioxidant. It is strong enough so that when it is used as a solvent, runs made at room temperature under strong illumination yield over 70% 1,2-dibromopropane, whether air is present or not. It is, however, noteworthy that glacial acetic acid becomes less effective in repressing the formation of 1,3-dibromopropane at 5° (Table X) where reactions run under the same illumination yield from 40–75% of the 1,3 dibromide (depending on the intensity of the illumination), a result quite at variance with the usual effect of decreased temperature, which is to favor the normal addition to give 1,2-dibromopropane.

These unusual results may be accounted for in either of two ways, dependent upon whether we assume that glacial acetic acid is as efficient an antioxidant at 5° in the light as it is at 30°.

(1) If we assume that the antioxidant properties of the acid are unimpaired at low temperatures, then we believe that there is no escape from the conclusion that visible and ultraviolet light slowly convert allyl bromide into a form which adds hydrogen bromide to give 1,3-dibromopropane even in the absence of peroxides. At room temperature, illumination could not greatly influence the composition of the addition products, since the rate of the normal addition is so high that reaction is complete before much conversion has occurred. At the lower tempera-

ture, however, where the rate of the normal reaction is low, the amount of conversion is greater and the proportion of the 1,3-dibromopropane formed is correspondingly increased.

(2) On the other hand, an explanation consistent with all the facts is that the antioxidant effect of the acetic acid decreases with the temperature (that it increases with the temperature is shown by No. 197 in Table X), and that light exaggerates the peroxide effect at all temperatures. That there is at least some peroxide effect in the light in glacial acetic acid at 5° is shown by the last two runs in Table X. The difference in yields is significant even if the difference in products is not. This viewpoint finds further corroboration in the addition of hydrogen bromide to allyl bromide in the absence of solvents and the presence of antioxidants in the light (Tables XIV and XV). The use of diphenylamine and hydroquinone at room temperature had a slight but decided effect with full illumination and a much larger effect with light of longer wave lengths in increasing the yield of 1,2-dibromopropane formed. A more powerful antioxidant, thiocresol, increased the yield of this product to 35% with full illumination. Under the combined effects of lowering the temperature of reaction to 5° and the use of this antioxidant, the yield of 1,2-dibromopropane was increased to 61%. This last result is in agreement with our other observations that the effectiveness of peroxides decreases with lowering of temperature. These results from Tables XIV and XV point to the conclusion that the yield of 1,3-dibromopropane could be still further decreased by the use of still better antioxidants.

*The results discussed in the preceding paragraph strongly suggest that all the factors (including now the light effect) which influence the addition of hydrogen bromide to allyl bromide exert their influence only through their effects on the minute but significant quantities of peroxides or oxygen present in the materials.*

6. **The Effect of Metallic Salts.**—The results of Table XVI (see also No. 329 in Table XII) show that anhydrous ferric and aluminum halides have a tremendous accelerating effect upon the normal addition. The velocity of the reaction is undoubtedly proportional to the amount of these metal salts present (*cf.* Nos. 320 and 365). Although the additions were allowed to proceed for six to eighteen hours at room temperature, we know definitely that they were complete long before that time. No. 333 was found to have reacted completely after eighteen hours at −75°, but we surmise from the vigorous boiling of the acetone–solid carbon dioxide bath fifteen or twenty minutes after the tube was put into it that the reaction was probably over in thirty minutes.

Copper salts have no effect on the direction of addition of hydrogen bromide to allyl bromide, but they may have a slight antioxidant and accelerating effect.

### TABLE XVI

### THE EFFECT OF IRON AND SOME IRON, ALUMINUM AND COPPER SALTS ON THE ADDITION OF HYDROGEN BROMIDE TO ALLYL BROMIDE

Except as noted otherwise, these addition mixtures contained 1.5 moles of hydrogen bromide, were dried and distilled onto the catalyst, and were run in the dark, at room temperature, and in the absence of air.

| No. | Catalyst | Moles of catalyst | Yield, % | Reaction, time | % 1,3-[b] | Remarks |
|---|---|---|---|---|---|---|
| 193 | Iron wire | 0.0011 | 50 | 42 hours | 18 | Iron did not dissolve |
| 320 | Anhydrous $FeCl_3$ | .007 | 100 | 6 hours | 7 | Mean of two results |
| 333 | Anhydrous $FeCl_3$ | .007 | 100 | 17 hours | 5 | Run at −75° |
| 365 | Anhydrous $FeCl_3$ | Trace[a] | 29 | 18 hours | 20 | |
| 331 | Hydrated $FeCl_3$ | 0.02 | 97 | 21 hours | 8 | Allyl bromide satd. with water at 0°. Bomb tube evacd. Reactn. mixt. not dried or distd. |
| 359 | Hydrated $FeCl_3$ | .009 | 93 | 17 hours | 8 | Reaction mixture not dried or distd. 0.027 mole $H_2O$ added. |
| 332 | Anhydrous $AlBr_3$ | .009 | 100 | 18 hours | 5 | |
| 194 | Cupric bromide | .00028 | 62 | 40 hours | 18 | |
| 380 | Cupric bromide | .01 | 83 | 11 days | 16 | |
| 310 | Cuprous bromide | .008 | 39 | 20 hours | 10 | |
| 381 | Cuprous bromide | .008 | 74 | 4 days | 16 | |

[a] A single minute crystal of ferric chloride (estimated to be about 0.000005 mole) was used. This small amount was sufficient, however, to impart a faint but distinct color to the reaction mixture. The other runs with the anhydrous salt were so darkly colored that they were opaque. [b] See corresponding note to Table I.

**7. The Effect of Surface Catalysts.**—The first two runs listed in Table XVII show that neither the glass surface nor materials within the glass affect the velocity of the reaction or the product formed. In the presence of silica gel and asbestos, however, the reaction is much faster

### TABLE XVII

### THE EFFECT OF SURFACE CATALYSTS UPON THE ADDITION OF HYDROGEN BROMIDE TO ALLYL BROMIDE

In all of these runs, 10 g. of allyl bromide containing 1.5 moles (10 g.) of hydrogen bromide was dried and distilled into the bomb tube containing the catalyst, and was sealed off without the entrance of air. The additions took place in the dark at room temperature.

| No. | Catalyst | Weight of catalyst, g. | Yield, % | Reaction, time | % 1,3-[b] | Remarks |
|---|---|---|---|---|---|---|
| 278 | None | | 87 | 9 days | 18 | From Table I, for comparison |
| 157 | Broken Pyrex | 20 | 85 | 9 days | 20 | |
| 263 | Glass wool | 1.6 | 79 | 7 days | 10 | |
| 264 | Asbestos[c] | 5.0 | 98 | 5 days | 10 | Mean of three results |
| 311 | Asbestos[d] | 5.0 | 77 | 18 hours | 8 | |
| 317 | Asbestos[e] | 4.3 | 71 | 67 hours | 15 | |
| 312 | Silica gel | 5–10 | 98 | 18 hours | 10 | |

[b] See corresponding note to Table I.

[c] Commercial acid-washed and ignited asbestos fiber.

[d] Material from same source extracted with concentrated hydrochloric acid for several days, washed, and dried.

[e] Same material used in run No. 311 washed, dried, and used over again.

but the composition of the product is unchanged. That this observed acceleration was due to iron salts was indicated by the deep red color of the reaction mixtures. Furthermore, when the asbestos was extracted with acid, the color produced was quite faint, and when this same asbestos was used over again a second time, there was no color in the presence of the reaction mixture and the yield was definitely less in four times the duration of the previous run, a fair indication that as iron salts were removed, the asbestos lost its activity. All of these runs point to the conclusion that the addition of hydrogen bromide to allyl bromide in the liquid phase is a homogeneous reaction.

## General Conclusions

The results described in this paper have certain bearings on the various general theories of addition to the double bond which have from time to time been advanced. Any such theory which neglects the effect of the peroxide content of the unsaturated compound can derive no support from the behavior of allyl bromide. In particular, the reactions of this substance are definitely at variance with the idea that the dielectric constant of the solvent controls the direction of addition. Further work (which will be published shortly) on allyl chloride, vinyl bromide, butene-1, propylene, and other unsaturated substances fully confirms the results herein described and indicates that the peroxide content of the unsaturated compound is at least an important, and probably the dominant, factor controlling the velocity and direction of many addition reactions. In fact, so widespread does the peroxide effect appear to be that most of the data recorded in the literature probably need to be revalued before they can be used for or against any general theory of addition. One thing at least is certain: before applying the reactions of any particular compound in favor of any theory, the question of whether or not the reactions of this compound are seriously affected by its peroxide content must first be decided.

The unusual results obtained in the study of the addition of hydrogen bromide to allyl bromide show the need of extension of work of this type to other olefins and other unsymmetrical reagents[12] as well as to conjugated systems. Work along these lines has been actively under way in this Laboratory for some time, and we hope to publish shortly our other findings.

## Experimental Part

**1. Removal of Allyl Bromide from Mixtures of 1,2- and 1,3-Dibromopropanes.**— It was planned in this work to determine the composition of the addition products by their indices of refraction. This method made necessary the removal of allyl bromide

---

[12] The unusual addition of mercaptans and of sodium and potassium alkyls to styrene may thus be viewed from an entirely new viewpoint. The addition reactions of this substance are now under investigation in this Laboratory.

from the dibromopropanes. The common methods for effecting similar removals were shown to be unsatisfactory when working with small quantities of materials. Even fractional distillation followed by washing with concentrated sulfuric acid and another fractional distillation was found to be inadequate for removing allyl bromide from a synthetic mixture of the two dibromopropanes, as shown by the index of refraction of the mixture.

The method finally adopted had its inception in the well-known activity of the bromine in allyl bromide as compared with that in the dibromopropanes. Many amines react quite rapidly with allyl bromide, the tertiary amines to give water-soluble substituted ammonium salts, while under the same conditions, no appreciable reaction takes place with the dibromopropanes. Dimethylaniline was the reagent chosen for our work to accomplish the removal of allyl bromide from 1,2- and 1,3-dibromopropanes, and its use is justified by the experiments in Table XVIII. Detailed directions concerning our use of this reagent will be given presently.

TABLE XVIII

THE REMOVAL OF ALLYL BROMIDE FROM THE DIBROMOPROPANES WITH DIMETHYLANILINE

A. 10.0 g. of a mixture of 1,2- and 1,3-dibromopropanes having $n^{20}_{\mathrm{D}}$ 1.5217 was mixed with 2.5 g. of allyl bromide. Several such mixtures were treated with dimethylaniline according to the standard procedure for different lengths of time to determine how much time was required for complete removal of the allyl bromide:

| | | | |
|---|---|---|---|
| Hours of treatment | 11 | 16 | 24 |
| $n^{20}_{\mathrm{D}}$ of product | 1.5172 | 1.5217 | 1.5216 |

B. A mixture having a composition by weight of the dibromopropanes corresponding to an index of refraction of 1.5215 was mixed with varying amounts of allyl bromide so that the total weight of each ternary mixture was 12.5 g. The allyl bromide was then removed according to the standard procedure:

| | | | | |
|---|---|---|---|---|
| Weight % of allyl bromide in ternary mixt. | 1 | 2 | 5 | 10 |
| $n^{20}_{\mathrm{D}}$ of mixture after removal of allyl bromide | 1.5216 | 1.5215 | 1.5214 | 1.5214 |

C. 10.0 g. each of mixtures of 1,2- and 1,3-dibromopropanes of different compositions were each mixed with 2.5 g. of allyl bromide which was then removed according to the standard procedure.

| Mixture no. | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| Mole fraction 1,3-, % | 5.3 | 28.9 | 55.2 | 76.2 | 94.7 |
| Mole fraction 1,2-, % | 94.7 | 71.1 | 44.8 | 23.8 | 5.3 |
| $n^{20}_{\mathrm{D}}$ calculated[a] | 1.5196 | 1.5204 | 1.5213 | 1.5221 | 1.5230 |
| $n^{20}_{\mathrm{D}}$ obsd. before addn. of allyl bromide | 1.5196 | 1.5205 | 1.5215 | 1.5223 | 1.5230 |
| $n^{20}_{\mathrm{D}}$ after addn. of allyl bromide, calcd.[a] | 1.5071 | 1.5078 | 1.5085 | 1.5091 | 1.5097 |
| $n^{20}_{\mathrm{D}}$ after removal of allyl bromide, obsd. | 1.5195 | 1.5205 | 1.5214 | 1.5222 | 1.5228 |

[a] Calculated on the assumption that the index of refraction of the mixture is a linear function of its composition.

We obtained the following indices of refraction of the pure dibromopropanes (Eastman Kodak Co. products): $n^{20}_{\mathrm{D}}$ 1,2-, 1.5194; 1,3-, 1.5232. The indices of refraction of mixtures of these two compounds is shown by Table XVIIIC to be a linear function of composition. Using an Abbé refractometer, it was possible to ascertain the composition of mixtures of these addition products within ±5%.

2. **Technique of Preparation of Reaction Mixture.**—Most of the work recorded in the literature, and the first two runs made by us, were made by repeated saturations of the allyl bromide with hydrogen bromide at about −10°. In the intervals between saturations, the mixtures were allowed to warm up to room temperature, or were heated.

This method is slow and time-consuming because of the low solubility of hydrogen bromide in allyl bromide at −10°.

To avoid these disadvantages, it was decided to dissolve sufficient hydrogen bromide in the allyl bromide in one step by cooling the allyl bromide to −75°. A simple apparatus (Fig. 3) was finally devised which enabled us also to exclude moisture and air, and which by a simple modification made it possible to introduce dry gases. The technique of carrying out an addition under these circumstances was as follows.

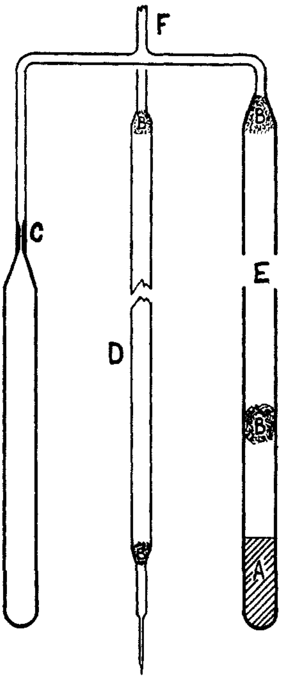


Fig. 3.—Apparatus used in drying and vacuum distillation of reaction mixtures. Pyrex glass used. A. Mixture of allyl bromide, hydrogen bromide and phosphorus pentoxide. B. Glass wool plugs. C. Piece of capillary tubing at which the receiver bomb tube is sealed off. D. Drying tube containing asbestos fiber and phosphorus pentoxide which is attached in this position when dried gases are to be admitted to the system after distillation. E. Bomb tube in which hydrogen bromide was dissolved in allyl bromide is sealed onto system at this point. F. Tube through which system is evacuated.

The required quantity (almost with exception, 10 g.) of allyl bromide was weighed out into the bomb tube shown at the right in Fig. 3. This tube was put into a freezing mixture at −75° and the necessary amount (10.0 g., 1.50 moles, except where noted) of dry hydrogen bromide gas was passed into the cold allyl bromide, care being taken to exclude moisture from the cooled tube. When the reaction was to be run in the presence of air, the bomb tube was simply sealed off at this point and put away. Otherwise the lower part of the bomb tube was immersed in liquid air, about a gram of phosphorus pentoxide was added, and a fairly tight-fitting glass wool plug was pushed into the tube as shown in Fig. 3. The rest of the apparatus shown was then sealed onto the top of this tube. The system was then evacuated to less than 3 mm. (often to less than 1 mm.), and at the same time all of the apparatus except that part of one bomb tube containing the reaction mixture was quickly heated with a hand torch to volatilize any moisture and gas that might be occluded on the inside walls. The connection to the pump was then sealed off without any gas entering the system. The contents were allowed to warm up to the temperature of a solid carbon dioxide freezing mixture, when they thawed out and were shaken gently with the phosphorus pentoxide for fifteen minutes or more at this temperature. The phosphorus pentoxide formed a finely dispersed, semi-gelatinous suspension in the liquid and settled only slowly after shaking.

The bomb tube containing the reaction mixture was then removed from the cooling bath and the other tube was put in so that the hydrogen bromide distilled over into the cooled bomb tube. The receiver was finally cooled in liquid air to bring over the allyl bromide. A vacuum distillation made in this way was fairly quiet, although bumping sometimes occurred with drying agents other than phosphorus pentoxide.

After the liquids were completely distilled off from the drying agent, which was not warmed at all, the receiver bomb tube was sealed off at the capillary tubing at its top. If capillary tubing were not used at this point, the seal sometimes blew in during sealing. Naturally, considerable pressures were developed when the bomb tubes reached room temperature, but the losses by explosion were less than 2%.

This technique seemed to meet quite well the necessary conditions imposed upon it. The apparatus had to be entirely of glass and without stopcocks, as lubricants and rubber might have contaminated the reaction mixtures. It was necessary also to dry the materials thoroughly and to remove them from the drying agent without any contact whatsoever with the atmosphere.

3. **Method of Completing Determinations.**—After the bomb tube had stood for the required time at the reaction temperature, it was cooled again in a solid carbon dioxide cooling mixture, opened by cracking with a hot wire at the top, and the contents were poured into a beaker of water. The product was then washed three times with water, dried with calcium chloride and distilled. Any high-boiling or polymerized products were eliminated by the distillation, but the quantities of these were always very small. The index of refraction of the distillate was then taken for the determination of the yield. The yields are calculated on the assumption that the index of refraction of a mixture of the dibromides with allyl bromide is a linear function of composition. The error involved in this assumption is small, as may be seen from Fig. 2.

The unreacted allyl bromide was then removed by the following procedure. Five cc. each of absolute alcohol and dimethylaniline were added, the whole shaken, and then allowed to stand at room temperature from seventeen to twenty-four hours. The absolute alcohol was added because in the preliminary trials described in Table XVIII, the quaternary ammonium salt formed from allyl bromide and the amine crystallized out of solution. Alcohol prevented the separation of this material, and although its use was unnecessary, the practice was continued for the sake of uniformity of procedure. After standing the required time at room temperature, the mixture was washed with 6-*N* sulfuric acid three times, with saturated bicarbonate solution once, and with water twice. The remaining dibromides were then dried over calcium chloride and distilled. The index of refraction of the mixture was then taken, and the composition of the addition product determined directly.

4. **Modifications for the Use of Solvents.**—In those runs in which solvents were employed, 1.5 moles of solvent was generally used to one mole of allyl bromide. Because the rate of reaction was usually slower, probably partly because of dilution of the reacting substances, more than the usual 1.5 moles of hydrogen bromide were often used, added in the manner mentioned previously. The only exception to this procedure was in the case of glacial acetic acid, which froze out if cooled very strongly at first. This difficulty was easily avoided by cooling the mixture gradually, for most of the acetic acid was soluble in the rest of the mixture at low temperatures after enough hydrogen bromide had been added. When the reaction mixture was to be dried and distilled *in vacuo*, the acetic acid and other solvents boiling above 100° were put into the receiver bomb tube directly and were not distilled. The same is true of antioxidants and catalysts.

Those solvents which could be removed by washing from the reaction mixture at the completion of the reaction were removed in this way. Solvents which were insoluble in water and which could not be conveniently removed by washing were removed by fractionation, for all of the solvents in this class which were used boiled below 100°, more than 40° below the lower-boiling of the addition products. For this separation a short fractionating column was used, and the distillate was rejected until the boiling point of the addition compound was nearly reached. The column was then allowed to drain completely and the residue was transferred to the miniature distilling flask always used, because too much material would have been lost in an attempt to distil all of the addition product through the column. After distillation, the residues were treated with dimethylaniline to remove remaining traces of allyl bromide and worked up thereafter according to the usual procedure.

5. **Estimation of Composition of Addition Products by Boiling Points.**—In many cases, comparison of the boiling range of an addition product with its index of refraction showed that the latter was in error, due to remaining traces of solvent or other added material, small amounts of by-products formed, or remaining traces of allyl bromide. Trouble from the last-named cause was encountered only when poor yields were obtained and insufficient dimethylaniline was used to remove the unchanged allyl bromide. On a few occasions, extremely warm and humid weather made accurate determination of refractive indices very difficult. In practically all cases, however, the error in index of refraction was small, less than one in the third decimal place, but this represents an error of about 26% in the composition of the addition product.

Toward the end of this work, a boiling point table was worked out very carefully, using as a basis runs made under the most favorable conditions where good yields were obtained. The construction of such a table was possible because the initial, final and some intermediate points of boiling ranges had been recorded for all of the distillations made. The use of such a table was valid because the same apparatus was always used for the distillations, because the latter were made at approximately equal rates with approximately equal quantities of material, because the table was based on mixtures of known composition, and because the difference between the boiling points of the two dibromopropanes was large, about 24°. Therefore our estimates of percentage composition are probably always accurate within 7 or 8%, and are usually within the limit of error involved in the determination of composition by index of refraction, ±5%. Because our table is purely empirical and of little value with other apparatus, its publication is omitted.

6. **Source of Allyl Bromide.**—Part of the allyl bromide employed in our work was purchased from the Eastman Kodak Co. The remainder was made very conveniently by a method suggested by Dewael[13] for the preparation of allyl chloride. 1.1–1.2 moles of gaseous hydrogen bromide was dissolved in pure allyl alcohol at 0° in the presence of 1–2% of cuprous bromide. Yields of 90–95% were obtained after the mixture had stood for a few hours at room temperature or at 10°. Allyl bromide from either source was further purified by washing with cold water, drying with sodium sulfate at −75° and distillation through a 1.5 meter column. The constants obtained were: b. p. (752 mm.) 69.6°; $n^{20}_{D}$ 1.4693.

7. **The Stability of Allyl Bromide and its Addition Products.**—Bromine was added to allyl bromide under a variety of conditions to show that there was no shift in the position of the double bond. The addition was performed in ordinary diffused light in ligroin, glacial acetic acid, 87% aqueous acetic acid and carbon disulfide, and without any solvent, and also 15 cm. from a 500-watt incandescent projection lamp in the last two cases. The products were all quite pure 1,2,3-tribromopropane, identified by freezing point, boiling point, and index of refraction.

The stability of both addition products toward light was demonstrated by exposing small samples of each to the light of a 100-watt frosted lamp for twenty-one hours. No change in index of refraction was noted. In another experiment, one-half mole of hydro-

---

(13) Dewael, *Bull. soc. chim. Belg.*, **39**, 40 (1930).

gen bromide was added to a small quantity of propylene bromide; the mixture was sealed into a bomb tube with air, and kept about 10 cm. from the same lamp for four days. No change in index of refraction or boiling point of the propylene bromide was found. This experiment shows that 1,3-dibromopropane, the product formed by the addition in the presence of light and air, is not the result of rearrangement of 1,2-dibromopropane under the experimental conditions of addition.

The authors wish to acknowledge their appreciation to Dr. James K. Senior for help in connection with the preparation of this manuscript.

## Summary

1. Methods have been developed for the study of the addition of hydrogen bromide to allyl bromide under carefully controlled conditions, removing the unchanged allyl bromide from the addition products, and for determining the yield and composition of the addition products by indices of refraction.
2. It has been shown that in the absence of oxygen and peroxides, hydrogen bromide adds very slowly to allyl bromide to give 1,2-dibromopropane, and that in the presence of small amounts of oxygen or peroxides, the addition is very rapid and the product is 1,3-dibromopropane.
3. The use of antioxidants has been introduced to eliminate the effect of peroxides on the addition.
4. The effects of catalysts have been investigated.
5. It has been shown that solvents, temperature, and probably illumination have no effect on the direction of addition of hydrogen bromide except in so far as these factors influence the peroxide effect. However, they may have a pronounced effect on the velocity of addition.
6. Work is actively under way in this Laboratory to ascertain how extensively the findings recorded in this paper may apply to other unsaturated compounds as well as to conjugated systems.

CHICAGO, ILLINOIS RECEIVED DECEMBER 2, 1932
PUBLISHED JUNE 6, 1933