# The Addition of Hydrogen Bromide to Allyl Bromide in the Presence of Various Substances. V. A Comparison of the Effect of Oxygen with That of Peroxide. The Relation between the Amount of Oxygen Present and the Result of Addition.

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Two groups of substances, oxygen and peroxides as one group and the ferro-magnetic metals as the other, have been found capable of not only inversing the proportion of 1,3-dibromopropane and 1,2-dibromopropane in the product from allyl bromide and hydrogen bromide but also increasing the total yield of the addition. While the catalytic action of the ferro-magnetic metals has been established exactly by the authors,(1) there has been no experimental evidence to decide whether the so-called peroxide effect is caused by oxygen or by peroxides or by both. But, as mentioned in the third paper of this series,(2) at least the effect by oxygen seems to be due to the action of molecular oxygen. The reason for it is given above all by the fact that the addition of hydrogen bromide to peroxide-free allyl bromide in the presence of oxygen in the dark gives mainly the abnormal addition product, 1,3-dibromopropane, while no peroxide can be formed from allyl bromide and oxygen in the dark as judged from the test with ammonium thiocyanate and ferrous ammonium sulphate, and hydrogen bromide can not be considered to facilitate the formation of a peroxide. The only possible alternative is to attribute the effect to a peroxide which might be formed even in the dark in such a minute quantity as not detected by the above-mentioned test.

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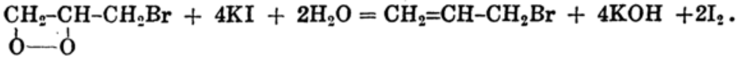
(1) Y. Urushibara and M. Takebayashi, this Bulletin, **11** (1936), 692, 754; **12** (1937), 51.

(2) Y. Urushibara and M. Takebayashi, this Bulletin, **11** (1936), 798.

*Corrections to the third paper*: All the numerical values of liberated bromine expressed in volumes of corresponding amounts of oxygen should be divided by 10. The mistakes were caused by errors in calculation. As the authors were then aware of some inevitable sources of errors involved in the estimation of bromine, they did not attach importance to the obtained figures, and discussions made in that paper and the conclusions drawn from them require no alteration nor modification. It has now become clear that only a small fraction of the oxygen in the air admitted into the reaction tube was consumed to oxidize hydrogen bromide in the presence of platinum black (exp. 1).

In Table 1 the results of additions to peroxide-containing allyl bromide in vacuum are compared with those of additions to peroxide-free allyl bromide in the presence of oxygen. Allyl bromide treated with oxygen was placed in diffused light for a few days for the formation of the peroxide. The peroxide content was determined by iodometry, assuming that all the oxygen atoms in the peroxide of allyl bromide are available for the oxidation of the iodide:



$$\underset{\text{O}}{\text{CH}_2}\text{—}\underset{\text{O}}{\text{CH}}\text{-CH}_2\text{Br} + 4\text{KI} + 2\text{H}_2\text{O} = \text{CH}_2\text{=CH-CH}_2\text{Br} + 4\text{KOH} + 2\text{I}_2.$$

The allyl bromide (24 g.) was taken in a reaction tube (135–140 c.c.). The contents were frozen by cooling in liquid air and the tube was evacuated, dissolved, uncombined oxygen being removed by this process. Then hydrogen bromide was condensed while the reaction tube was cooled in solid carbon dioxide and chloroform until a volume increase corresponding to 20 g. of hydrogen bromide was reached (total volume of the liquid 27 c.c.). The tube was evacuated again under cooling in liquid air and sealed off without entrance of air. On the other hand, in a quite similar manner, another reaction tube was charged with peroxide-free allyl bromide and hydrogen bromide, a volume of oxygen corresponding to the above peroxide content (the available peroxidic oxygen and the molecular oxygen equal in the number of atoms) being admitted at sealing. The tubes were shaken at room temperature in the dark for three days. In order that the reaction may occur under the same conditions, the additions to be compared were carried out simultaneously. Thus additions belonging to the same series occurred at the same time.

As allyl bromide (commercial product distilled once) used in exp. 2–4 was found not pure later, it was redistilled for exp. 5. In exp. 6–8 portions from the same specimen of especially purified allyl bromide were employed. The influence of impurities on the catalytic action of oxygen will be discussed later, but for the present more weight may be attached to the experiments of Series III.

Exp. 4 and 7 were carried out to see how quickly the peroxide is decomposed by the action of hydrogen bromide, allyl bromide being treated with hydrogen bromide in the reaction tube at room temperature for a short time before cooling in liquid air. The peroxide is decomposed rather rapidly, if not instantaneously. In the third paper(2) it was shown that the peroxide is not decomposed by hydrogen bromide at the temperature of solid carbon dioxide and chloroform, and that uncombined oxygen is removed by evacuation under cooling in liquid air.

Table 1. Comparison of Oxygen and Peroxide.

| Series of exp. | No. of exp. | Remarks | Product: Dibromopropanes | | | |
|---|---|---|---|---|---|---|
| | | | Yield (%) | Boiling point (°C/mm.) | 1,3- (%) | 1,2- (%) |
| I | 1 | Allyl bromide containing peroxide corresponding to 4.8 c.c. $O_2$ per 24 g. | 52 | 44-53.5/12 | 87 | 13 |
| | 2 | Peroxide-free allyl bromide. 4.8 c.c. $O_2$ admitted. | 53 | 44-54/12 | 95 | 5 |
| II | 3 | Allyl bromide containing peroxide corresponding to 0.9 c.c. $O_2$ per 24 g. | 28 | 41-52.5/11 | 62 | 38 |
| | 4 | The same allyl bromide as above, treated with HBr for 2 min. at room temp. and left to stand for 10 min. before condensing HBr. | 16 | 36-49/11 | 26 | 74 |
| | 5 | Peroxide-free allyl bromide. 0.9 c.c. $O_2$ admitted. | 57 | 43-52.5/11 | 81 | 19 |
| III | 6 | Allyl bromide containing peroxide corresponding to 0.8 c.c. $O_2$ per 24 g. | 43 | 42-53.5/10 | 70 | 30 |
| | 7 | The same allyl bromide as above, treated with HBr for 1 min. at room temp. and HBr condensed immediately. | 35 | 41-53/10 | 65 | 35 |
| | 8 | Peroxide-free allyl bromide. 0.8 c.c. $O_2$ admitted. | 46 | 42-53.5/10 | 78 | 22 |

Experiments of each series were carried out simultaneously. The peroxide content of allyl bromide is given in the volume of the corresponding amount of oxygen for the temperature and pressure at which oxygen was taken in the run for comparison.

Table 2. Relation between the Amount of Oxygen Present and the Result of Addition.

| Series of exp. | No. of exp. | Volume of oxygen admitted (c.c.) | Product: Dibromopropanes | | | |
|---|---|---|---|---|---|---|
| | | | Yield (%) | Boiling point (°C./mm.) | 1,3- (%) | 1,2- (%) |
| IV<br>Purified allyl bromide.<br>Time of reaction: 3 days. | 9 | 0 | 14 | 32-36/10 | 4 | 96 |
| | 10 | 0.5 | 21 | 34-46/10 | 38 | 62 |
| | 11 | 1.5 | 44 | 42-51.5/9 | 95 | 5 |
| | 12 | 2.5 | 53 | 42-51.5/9 | 96 | 4 |
| V<br>Purified allyl bromide.<br>Time of reaction: 5 days. | 13 | 0 | 24 | 35-42/10 | 12 | 88 |
| | 14 | 0.5 | 37 | 37-51/10 | 60 | 40 |
| | 15 | 1.5 | 56 | 42-51.5/9 | 96 | 4 |
| | 16 | 2.5 | 62 | 42-51.5/9 | 96 | 4 |
| VI<br>Once distilled allyl bromide.<br>Time of reaction: 5 days. | 17 | 0 | 28 | 38-47/13 | 44 | 56 |
| | 18 | 0.5 | 64 | 45-56.5/13 | 89 | 11 |
| | 19 | 1.5 | 68 | 45-56.5/13 | 96 | 4 |
| | 20 | 2.5 | 73 | 45-56.5/13 | 96 | 4 |

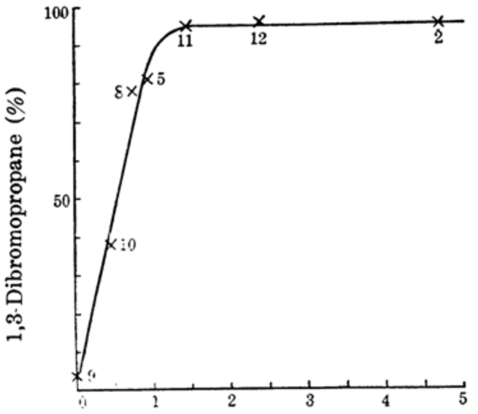


Fig. 1. Series IV (Exp. 9–12). Exp. 2, 5, and 8.

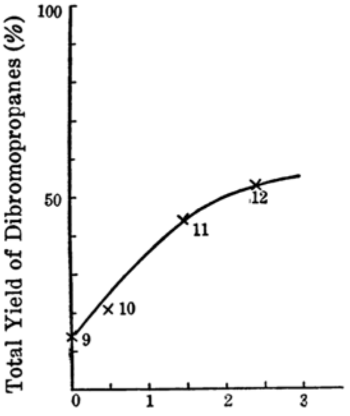


Fig. 2. Series IV (Exp. 9–12).

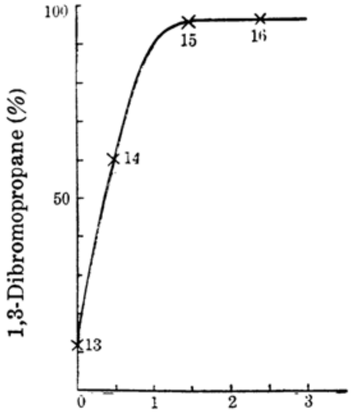


Fig. 3. Series V (Exp. 13–16).

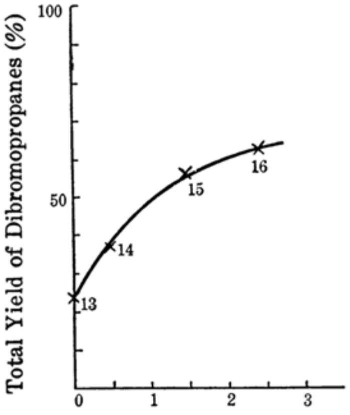


Fig. 4. Series V (Exp. 13–16).

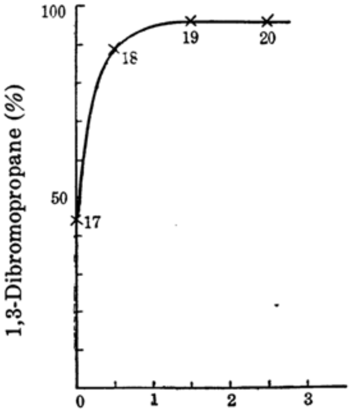


Fig. 5. Series VI (Exp. 17–20).

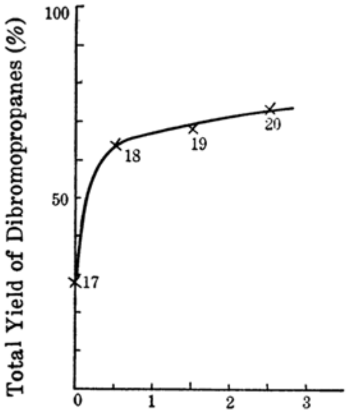


Fig. 6. Series VI (Exp. 17–20).

From Table 1 it can be seen that both the total yield of the product and the proportion of 1,3-dibromopropane in the product are greater in additions with peroxide-free allyl bromide in the presence of oxygen than in the additions with peroxide-containing allyl bromide in vacuum. On the one hand, part of oxygen introduced in gas into the reaction tube may be dissolved by the liquid and part of the dissolved oxygen may be transformed into a peroxide (one molecule from one). On the other hand, the peroxide may gradually decompose to liberate oxygen (one molecule from one) and part of the generated oxygen may leave the liquid. No matter how fast these changes may proceed, and no matter whether or not the changes from both sides go so far as to attain sooner or later the same equilibrium state, both the amount of peroxide alone and the total amount of the peroxide and molecular oxygen in the liquid where the addition takes place must be always greater in the experiments with peroxide-containing allyl bromide than in the experiments with peroxide-free allyl bromide. Such must be the case even if only one half of oxygen in the peroxide were liberated as molecular oxygen on decomposition, because then it could be much more naturally taken for granted that also one half of oxygen would be available in iodometry. In this connection it may be pointed out that neither oxygen nor peroxide oxidizes hydrogen bromide during the addition reaction with allyl bromide, but both do in the presence of platinum black.(2)

Under these circumstances the peroxide effect still appeared more marked in the additions with peroxide-free allyl bromide in the presence of oxygen. This observation permits to draw the following conclusions: (1) Molecular oxygen possesses catalytic activity in the sense of the so-called peroxide effect; and (2) the catalytic activity of the peroxide, if any, is smaller than that of molecular oxygen. It can not be decided, however, whether the peroxide is active at all or not. The fact that, while the action of oxygen is very regular as shown also by the experiments described below, the action of the peroxide is rather irregular as seen from Table 1, suggests the possibility that the peroxide exerts catalytic action not directly but through molecular oxygen generated by its decomposition. It must be taken into consideration that the peroxide is decomposed by hydrogen bromide rather quickly (exp. 4 and 7).

The above conclusions exclude the assignment of any catalytic effect to an undetectable amount of the peroxide and the effect observed with oxygen must be wholly due to the action of molecular oxygen.

Table 2 and the accompanying figures show the results of three series of additions with peroxide-free allyl bromide in the presence of various volumes (0, 0.5, 1.5, and 2.5 c.c.) of oxygen. The capacities of the reaction tubes were 135–140 c.c. and the total volume of the reacting liquid (allyl bromide and hydrogen bromide) was 27 c.c. in condensed state. The experimental procedure was the same as described above, except that respective volumes of oxygen were admitted at sealing after evacuation. Purified allyl bromide was used in Series IV and V, and once distilled commercial product in Series VI. The time of reaction was 3 days in Series IV, and 5 days in Series V and VI. Additions to be related to one another were carried out as simultaneously as possible. For Series IV and V volumes of oxygen corrected to the normal temperature and pressure were used in the figures.

An experimental procedure as described above does not allow of taking an exact amount of hydrogen bromide nor of controlling the temperature at all. Moreover, the yield is calculated by weighing the dibromopropane mixture really obtained through routine processes for preparation involving the removal of unchanged allyl bromide with dimethylaniline. Hence, the numerical values of yields could not be expected to be exact nor even to be comparable with one another. Nevertheless, it can be seen that the yield increases with the amount of oxygen and with the time of reaction, and is greater in additions with impure allyl bromide than in additions with pure allyl bromide.

On the other hand, it is possible to make more exact mention of the relation between the amount of oxygen and the composition of the product. When the amount of oxygen is 1.5 c.c. and more, the proportion of 1,3-dibromopropane in the product is constant at about 95%, irrespective of the time of reaction and the purity of allyl bromide. In exp. 2 where once distilled allyl bromide was used as in exp. 17–20, and oxygen as much as 4.8 c.c. was admitted, the proportion of 1,3-dibromopropane was 95% (see Fig. 2). Also in the range of less than 1.5 c.c. of oxygen the three series are qualitatively similar: the proportion of 1,3-dibromopropane increases rapidly with the increase of oxygen. In this region, however, the formation of 1,3-dibromopropane is favoured slightly by the longer time of reaction and greatly by the presence of impurities. It is worthy of note that, although the yields of exp. 5 and 8 carried out with purified allyl bromide deviate from the curve of Fig. 2, the proportions of 1,3-dibromopropane come well into line with the results of Series IV (Fig. 1).

Exp. 2 falls in the region where impurities do not affect the composition of the product, which justifies the comparison of it with exp. 1. Allyl bromide was purer in exp. 5 than in exp. 3, and, therefore, a comparison as made above is reasonable. Exp. 6, 7, and 8 were carried out with portions from the same purified specimen, and they are quite comparable.

As mentioned above, impurities in allyl bromide influence the catalytic action of oxygen, exaggerating both the inversing effect on the direction of addition and the increasing effect on the yield of the product. But there has been no indications to the possibility that impurities may play the leading part in the so-called peroxide effect.

In this way the action of oxygen has been established. The next problem is to decide whether the catalytic action of oxygen is homogeneous (dissolved oxygen acting) or heterogeneous (oxygen adsorbed on the glass wall coming into play). Experiments devised for the solution of this problem are now under way.

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