THE ADDITION OF HYDROGEN BROMIDE TO ALLYL BROMIDE IN THE PRESENCE OF VARIOUS SUBSTANCES.
III. A CONTRIBUTION TO THE ELUCIDATION OF THE SO-CALLED PEROXIDE EFFECT.

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The experiments described in this paper have been carried out with a view to elucidating the nature of the so-called peroxide effect in the addition of hydrogen bromide to allyl bromide. For the introduction to the present work the previous papers⁽¹⁾ may be consulted with.

The general procedure was as follows (compare the previous papers). Platinum black contained in the reaction tubes was heated at 250° in vacuum and then washed with hydrogen bromide gas. Allyl bromide (24 g. or 0.2 mol) was poured into the reaction tubes, which were filled beforehand with hydrogen bromide gas in experiments with platinum black. Then hydrogen bromide was introduced into the tubes cooled with solid carbon dioxide and chloroform, until the volume increase of the liquid reached 10 c.c. corresponding to 20 g. or 0.25 mol of hydrogen bromide. In exp. 1 allyl bromide and hydrogen bromide collected in the mixing tube were distilled in vacuum into the reaction tube as in the previous experiments.⁽²⁾ The mixtures were sealed in vacuum under cooling in liquid air. In exp. 1 air was allowed to enter the tube before sealing. The tubes were slipped into iron pipes and shaken at room temperature for three days. The contents were then treated as previous. Other particulars to individual cases will be given below. The results are shown in the accompanying table. The general decrease in the yields of the products compared with those obtained previously may be attributed to the fall of the room temperature.

The combined effects of platinum black and air were observed in exp. 1. The result, being very reasonable considering the results obtained with platinum black alone and with air alone (see the first paper), may be considered to represent simply the consequence of the competition of the two catalysts. Bromine was liberated, and its amount was roughly estimated to correspond to 45 c.c. of oxygen (2 Br : O) by the colorimetry of the wash

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(2) As treated allyl bromide was used in all other experiments recorded in this paper, the distillation process was discarded.

No. of exp.	Treatment of allyl bromide and amount of Pt black, if added.	Products: dibromopropanes				Volume (c.c.) of O_2 corresponding to liberated bromine
		Yield (%)	Boiling point (°C./mm.)	1, 3- (%)	1, 2- (%)	
1	Peroxide-free allyl bromide. Pt black 1.0 g. Air present.	30	38–49/16	39	61	45 (colorimetry)
2	Allyl bromide used immediately after passing O_2 for six hours.	15	32–38/14	4	96	—
3	The same allyl bromide as 2. Pt black 0.5 g.	30	36–47.5/14	33	67	35 (colorim.)
4	Allyl bromide treated with O_2 and placed in diffused light.	25	38–53.5/11	57	43	—
5	The same allyl bromide as 4. Pt black 0.5 g.	24	38–46/12	41	59	49 (iodometry) 48 (colorim.)
6	Allyl bromide treated with O_2 and placed in diffused light.	41	40–55.5/12	70	30	—
7	The same allyl bromide as 6. Uncombined O_2 removed. Pt black 0.5 g.	34	38–54.5/11	39	61	43 (iodom.) 36 (colorim.)

water of the reaction mixture against a standard bromine water. In experiments with peroxide-free allyl bromide, neither platinum black alone nor air alone has ever produced bromine from hydrogen bromide during the reaction.

A mixture of dibromopropanes (refractive index 1.5225,1,3-compound 84%) (0.1 mol) was shaken with hydrogen bromide (0.1 mol), platinum black (0.5 g.), and dry air, by the same procedure as in the experiments of addition. The refractive index of the dibromopropane mixture was not changed by this treatment. The amount of bromine liberated corresponded to 14 c.c. of oxygen by colorimetry. This experiment shows that dibromopropanes are not isomerized by the action of any of platinum black, oxygen, and hydrogen bromide, and that bromine is produced from hydrogen bromide by the action of oxygen and platinum black even in the absence of the unsaturated compound, allyl bromide, the intermediate formation of a peroxide being unnecessary for the oxidation of hydrogen bromide.

The authors have made an interesting observation on the formation of a peroxide in allyl bromide. Even after oxygen was passed into allyl bromide for six hours, the peroxide reaction with ammonium thiocyanate and ferrous ammonium sulphate was given only very slightly. When hydrogen bromide was added to allyl bromide treated with oxygen in this way, the result was quite normal (exp. 2),(3) that is to say, the same as with untreated allyl bromide. Thus it was shown that oxygen was not combined with allyl bromide by mere passing of the former into the latter, and that, on introducing hydrogen bromide into allyl bromide at the temperature of solid carbon dioxide mixed with chloroform and then evacuating the mixture under cooling in liquid air, oxygen dissolved in allyl bromide was totally driven out. Nevertheless, when platinum black was put in the reaction tube beforehand and the addition was effected in the same way, a result similar to exp. 1 was obtained, bromine liberated corresponding to 35 c.c. of oxygen by colorimetry (exp. 3).(3) The authors consider that the oxygen once dissolved in allyl bromide was retained by platinum black in some way or other at the low temperatures and given off again into the reaction mixture at room temperature. This assumption is supported by the fact that allyl bromide giving an intense colouration with ammonium thiocyanate and ferrous ammonium sulphate lost entirely the peroxide reaction on shaking with platinum black at room temperature for a few hours, showing that platinum black catalyzes the decomposition, rather than the formation, of the peroxide, and thus excluding the possibility of the fixation of oxygen by allyl bromide in the form of a peroxide with the aid of platinum black.

Now it has been found that light plays an important role in the formation of a peroxide in allyl bromide. Allyl bromide treated with oxygen in the dark for six hours did not give the peroxide reaction at all. When allyl bromide treated with oxygen was kept in diffused light for a few days, it gave an intense colouration with ammonium thiocyanate and ferrous ammonium sulphate, while a control substance (a portion of the allyl bromide treated with oxygen) placed in the dark during the same period gave no colouration and even after a month's standing in the dark at room temperature produced not the slightest peroxide reaction. The outdoor diffused light was naturally more effective for the peroxide formation than indoor light, but the direct sunlight caused the polymerization of allyl bromide. On adding hydrogen bromide to allyl bromide giving the peroxide reaction, uncombined oxygen being removed by evacuation under cooling in liquid air before (exp. 6)(3) and after (exp. 4)(3) the introduction of hydrogen bromide,(4) the abnormal addition

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(3) Exp. 2 and exp. 3 were carried out simultaneously with portions from the same specimen of treated allyl bromide; so were done exp. 4 and exp. 5; also exp. 6 and exp. 7. The difference in the yields between the last two groups of experiments may be, at least partly, due to the different temperatures of the room.

(4) In exp. 6 the tube was evacuated as usual also at sealing.

product (1,3-dibromopropane) undoubtedly predominated over the normal (1,2-dibromopropane). In exp. 5(3) hydrogen bromide was added to allyl bromide containing the peroxide (and also uncombined oxygen) in the presence of platinum black, the mixture being evacuated only at sealing. In exp. 7,(3) uncombined oxygen was removed from allyl bromide contained in a side tube provided especially for this purpose by evacuation under cooling in liquid air, and allyl bromide treated in this way was decanted in vacuum into the reaction tube containing platinum black. The results of exp. 5 and exp. 7 were similar to exp. 1, bromine being liberated in amounts shown in the table.

The results described above give an important suggestion, As mentioned above, a peroxide is formed from allyl bromide and oxygen only under the action of light, while the addition to peroxide-free allyl bromide in the presence of oxygen in the dark gives mainly 1,3-dibromopropane. Thus it is very probable that the effect may be attributed to the action of oxygen itself and not to any formed peroxide, because neither hydrogen bromide nor dibromopropanes can be considered to be capable of producing a peroxide from allyl bromide and oxygen. Moreover, platinum black possessing the power of decomposing peroxides and of accelerating the normal addition can not totally suppress the so-called peroxide effect by oxygen (exp. 1), allowing the formation of about 40% 1,3-compound. It may be rather suspected that peroxides are active because of the generation of oxygen by their decomposition, whether platinum black is present or not. In this connection it may be added that peroxide-containing allyl bromide had lost in fact the peroxide reaction after the action of hydrogen bromide, both in the presence and in the absence of platinum black. Experiments devised to furnish more definite indications on these points are now under way.

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