THE ADDITION OF HYDROGEN BROMIDE TO ALLYL BROMIDE IN THE PRESENCE OF VARIOUS SUBSTANCES. I.

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One of the authors (Urushibara) observed that in the absence of foreign substances hydrogen bromide adds to undecenoic acid $CH_2=CH-(CH_2)_8-COOH$ in toluene solution to give 10-bromo-undecoic acid $CH_3-CHBr-(CH_2)_8-COOH$ mainly, while in the presence of a trace of something coming from air the product was nearly pure 11-bromo-undecoic acid $CH_2Br-CH_2-(CH_2)_8-COOH$.(1) At that time the effect was attributed to the action of moisture. On the subsequent appearance of the paper of M. S. Kharasch and F. R. Mayo,(2) Professor R. Robinson of Oxford (private communication) pointed out that further experiments were required before it could be decided whether the active catalyst was really moisture or, as hitherto unsuspected, the oxygen of the air. According to Kharasch and Mayo, in the absence of oxygen and peroxides or in the presence of an antioxidant such as diphenylamine hydrogen bromide adds slowly to allyl bromide $CH_2=CH-CH_2Br$ (in the dark at room temperature in the absence of solvents) to give mainly 1,2-dibromopropane $CH_3CHBrCH_2Br$ (the normal addition), while in the presence of oxygen or a peroxide such as benzoyl peroxide the addition is rapid and the product consists mainly of 1,3-dibromopropane $CH_2BrCH_2CH_2Br$ (the abnormal addition). The effect is called the peroxide effect. Subsequently R. Ashton and J. C. Smith(3) found that the substance which came from air and influenced the direction of addition of hydrogen bromide to undecenoic acid was also oxygen. Several papers on the effect of oxygen and peroxides on the addition of hydrogen bromide to the ethylenic linkage have since been published.(4)

The experiments described in the present paper have been carried out to investigate the effects of various substances other than oxygen and peroxides

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(1) Report of the discussion of the Chemical Society of London (March 2nd, 1933), *J. Soc. Chem. Ind.*, **52** (1933), 219.

(2) *J. Am. Chem. Soc.*, **55** (1933), 2468.

(3) *J. Chem. Soc.*, **1934**, 435.

(4) M. S. Kharasch and co-workers, *J. Am. Chem. Soc.*, **55** (1933), 2521, etc.; R. P. Linstead and H. N. Rydon, *J. Chem. Soc.*, **1934**, 2001; P. L. Harris and J. C. Smith, *J. Chem. Soc.*, **1935**, 1108, 1572.

on the direction of addition of hydrogen bromide to allyl bromide and on the yield of the products. The results are summarized in the accompanying table.

No. of experiment	Substance	Amount added (g.)	Specific susceptibility (χ)	Products			
				Yield (%)	Boiling point (°C./mm.)	Composition (%)	
						1,3-Dibromo-propane	1,2-Dibromo-propane
1	None			20	40–41/18	7	93
2	Oxygen (air)	—	$+107.7\times10^{-6}$	35	57–61/18	93	7
3	Sulphur	0.03	-0.34×10^{-6}	15	40–42/17	17	83
4	Nitric oxide	—	$+0.48\times10^{-6}$	23	40–41/17	12	88
5	Reduced iron	3.4	ferro-magnetic	36	54–64/21	71	29
6(5)	,,	3.4	,,	37	54–64/21	73	27
7	Reduced nickel	3.5	,,	36	52–67/24	68	32
8(5)	,,	3.5	,,	34	48–67/24	63	37
9	Platinum black	0.7	$+1.1\times10^{-6}$	34	44–45/20	12	88
10(5)	,,	1.0	,,	35	44–46/22	4	96
11	$FeBr_2$ (anhydrous)	2.0	—	20	44–45/21	7	93
12	$MnSO_4$ (anhydrous)	2.0	$+114\times10^{-6}$	15(6)	44–45/21	7	93

The experimental procedure, the treatment of the reaction products, and the method of the determination of the proportion of 1,2-dibromopropane and 1,3-dibromopropane were practically the same as described by Kharasch and Mayo. All the substances used as catalysts were carefully prepared. Just before use, reduced iron, reduced nickel, and platinum black, contained in the reaction tubes, were heated at 250° in vacuum for an hour and then washed with pure hydrogen bromide gas three times. Other solid substances were treated in vacuum at room temperature. Allyl bromide (24 g. or 0.2 mol) and hydrogen bromide (20 g. or 0.25 mol) were collected in air- and moisture-free state in the mixing tubes cooled in solid carbon dioxide and chloroform. The reaction tubes and the mixing tubes were then connected by fusion after filled with hydrogen bromide gas. The whole system was immediately evacuated, while the mixing tubes were cooled in liquid air, and then the contents of the mixing tubes were distilled into the reaction tubes by cooling the latter in liquid air. Nitric oxide, carefully prepared and freed from oxygen by solidification and evacuation, was passed into the mixture of allyl bromide and hydrogen bromide before distillation. When the distillation was over, the reaction tubes were sealed off without the entrance of air. In ex-

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(5) The reaction tube was shaken during daytime.

(6) Fraction boiling over 100°/21 mm. : 3%.

periment 2 (see the table) air was allowed to enter the tube before sealing. The tubes were placed in a bomb-furnace, or shaken in an iron pipe during daytime, in the dark at room temperature for three days. Then the contents were treated according to the directions of Kharasch and Mayo, the composition of the addition products being determined by the refractive indices. The yields shown in the table were, however, calculated in percentages to the theoretical value from the weights of the products.

The reaction mixture dissolved sulphur totally, ferrous bromide partially, but not other solid substances. Iron and nickel seemed to be attacked slightly by hydrogen bromide, although no change was observed in appearance of the catalysts after the reaction.

Sulphur and nitric oxide show only a small influence, if any, on the direction of addition and on the yield of the products. A similar result with nitric oxide was obtained by Ashton and Smith in the addition of hydrogen bromide to undecenoic acid. Reduced iron, reduced nickel, and platinum black all increase the total yields of the products, but the ferro-magnetic metals influence the direction of addition to produce much more 1,3-dibromopropane than 1,2-dibromopropane like oxygen, their catalytic action being selective, while the para-magnetic platinum seems to accelerate both the normal and the abnormal additions. The fact that ferrous bromide influences neither the direction of addition nor the yield of the products affords an evidence for attributing the effect of the reduced iron to the action of the metallic iron itself and not to ferrous bromide which may be formed by the attack of hydrogen bromide. Kharasch and Mayo added hydrogen bromide to allyl bromide in the presence of iron wire in the experiments on the effect of iron salts, but the catalyst probably happened to be not sufficient in quantity and still less in the surface area for detecting the action of the metal. Manganous sulphate manifests practically no influence on the direction of addition.

The additions in the presence of the ferro-magnetic catalysts and diphenylamine have given results similar to those of the experiments with the same metals but without the antioxidant. The details will follow.

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