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

FURTHER EXPERIMENTS ON THE EFFECTS OF FERRO-MAGNETIC CATALYSTS.

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In the absence of oxygen and peroxides or in the presence of an antioxidant such as diphenylamine hydrogen bromide adds slowly to allyl bromide and the product consists mainly of 1,2-dibromopropane (the normal addition), while in the presence of oxygen or a peroxide such as benzoyl peroxide the addition is rapid and 1,3-dibromopropane is mainly produced (the abnormal addition).(1) As reported in the previous paper(2) the authors found that the ferro-magnetic metals, iron and nickel, exert an influence similar to that of oxygen and peroxides on the addition of hydrogen bromide to allyl bromide, accelerating the abnormal addition. The experiments recorded in this paper have been carried out further to investigate the effects of ferro-magnetic substances on the addition of hydrogen bromide to allyl bromide. The experimental procedure and the conditions of addition were all the same as in the experiments recorded in the previous paper. The catalysts were heated at 250° in vacuum for an hour and then washed with pure hydrogen bromide gas. Each addition was carried out with 24 g. or 0.2 mol of allyl bromide and 20 g. or 0.25 mol of hydrogen bromide. The accompanying table shows the results of additions in the dark at room temperature in the absence of solvents and air, reaction time being three days.

Although, in the previous experiments on the effects of iron and nickel, peroxide-free allyl bromide was used and air was excluded, experiments were repeated with the addition of diphenylamine (0.5 g.), other conditions being unaltered. As shown in the table (experiments 1,2, and 4), the results are quite similar to those obtained without the antioxidant (compare the table in the previous paper). Therefore, the effect observed in the experiments with the ferro-magnetic metals can be undoubtedly attributed to the metals, and the possibility of the participation of oxygen or peroxides which might have been present by any chance can be excluded.

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(1) M.S. Kharasch and F.R. Mayo, *J. Am. Chem. Soc.*, **55** (1933), 2468.

(2) This Bulletin, **11** (1936), 692.

No. of exp.	Catalyst and amount added (g.)	Products				Remarks
		Yield (%)	Boiling point (°C./mm.)	Dibromo-propanes (%)		
				1,3-	1,2-	
1	Reduced iron 3.4	39	53–65/22	78	22	Diphenylamine 0.5 g. Shaken
2	,, ,,	33	48–62/18	71	29	Diphenylamine 0.5 g.
3	,, ,,	35	50–65/22	68	32	Magnetic field (5700 gausses) applied
4	Reduced nickel 3.5	32	45–58/16	58	42	Diphenylamine 0.5 g. Shaken
5	,, ,,	37	45–54/23	17	83	Nickel placed in air for 5 weeks after preparation Shaken
6	Reduced cobalt 3.5	42	38–43/16	7	93	Commercial cobalt Diphenylamine 0.5 g. Shaken
7	,, ,,	40	37–50/15	30	70	Freshly reduced cobalt Diphenylamine 0.5 g. Shaken
8	Iron-sand 4.6	47	45–48/24	12	88	Shaken
9	,, ,,	44	45–48/23	7	93	

All the additions recorded in the present and the previous papers took place in Pyrex glass tubes placed in a bomb-furnace or in an iron pipe, except experiment 3, where the Pyrex tube was placed in a magnetic field of about 5700 gausses, although the intensity of the field was far too small to expect any effect. The results are well within the range of the results obtained without the magnetic field.

If iron and nickel act as surface catalysts in the addition of hydrogen bromide to allyl bromide, their action must be governed by the conditions of the surface. In experiment 5, reduced nickel, which had been placed in air for five weeks after preparation and had taken a brown colour, was used. In this case, the effect of the metallic nickel on the direction of addition was far repressed. The good yield of the addition products may be attributed to the action of nickel oxide or bromide. In all other experiments with nickel the freshly reduced metal was used. In experiments with iron, the commercial reduced iron (Kahlbaum) was employed throughout. Thus it cannot be certain that the surface was clean from the oxide of iron. The oxide of iron would react with hydrogen bromide yielding ferric bromide. Ferric chloride is known by Kharasch and Mayo to possess a tremendous accelerating effect upon the normal addition⁽³⁾. Therefore, if freshly reduced iron is used, effect of the metal may appear more conspicuous.

Cobalt was attacked by hydrogen bromide to a great extent, and a green solid substance was formed in the reaction mixtures, covering the metal. On this account, with commercial reduced cobalt (Kahlbaum) no effect (experiment 6), and even with freshly reduced cobalt but a slight effect (experiment 7), on the direction of addition were observed. The remarkable increasing effect on the yields of the products may be attributed to the action of the cobalt salt.

With a view to testing a strongly magnetic compound, iron-sand was used (experiments 8 and 9). The formation of a considerable amount of ferric bromide was shown by the intense brown colour of the reaction mixtures, and in accordance with it the yields of the reaction products were extremely increased without any marked influence on the composition of the products.

Further the authors have obtained some interesting results in the experiments with platinum black and oxygen or peroxides. The details will follow.

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(3) *Loc. cit.* see p. 2489.