The Addition of Hydrogen Bromide to Allyl Bromide in the Presence of Various Substances. IV. The Effect of the Ferro-magnetic Metals Free from Oxides. Remarks on the Catalytic Action of the Ferro-magnetic Metals and Oxygen.

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The authors have found that the ferro-magnetic metals in such forms as reduced iron and reduced nickel influence the addition of hydrogen bromide to allyl bromide in the same way as oxygen and peroxides :(1) In the presence of reduced iron or reduced nickel, hydrogen bromide adds rapidly to allyl bromide (in the dark at room temperature in the absence of solvents, oxygen, and peroxides) and the greater part of the product is the abnormal addition product 1,3-dibromopropane, while in the absence of foreign substances the addition is slow and proceeds mainly to the formation of the normal product 1,2-dibromopropane. A difference, however, exists between these two groups of catalysts in that, while the influence of oxygen or peroxides is totally eliminated by

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(1) The first paper of this series, this Bulletin, **11** (1936), 692.

the addition of an antioxidant such as diphenylamine, the effect of the ferro-magnetic metals undergoes no modification in the presence of the antioxidant.(2) Now, with a special precaution of removing traces of oxides from the reduced metals, the ferro-magnetic metals have been found more effective in the sense of the predomination of 1,3-dibromopropane in the product of addition of hydrogen bromide to allyl bromide than in the previous experiments carried out with no such precaution.

In the previous experiments with freshly reduced nickel the percentage of 1,3-dibromopropane in the addition product was found 68(1), 63(1), and 58(2). Reduced nickel used in those additions was prepared under the conditions suitable for the preparation of the hydrogenating catalyst by passing pure hydrogen gas over nickel oxide (Kahlbaum, "cobalt free") heated at 300–400°. Reduction might possibly be incomplete at this temperature, and, moreover, the metal reduced in this way evolved heat when taken to the air. Thus it may be suspected that even freshly reduced nickel was not free from traces of oxides.(3) As it was really found that the power of accelerating the abnormal addition is far diminished by keeping reduced nickel long in the air,(2) it seemed very important to examine the effect of reduced nickel free from oxides. For this purpose nickel oxide was reduced at a higher temperature (dull red-heat). The metal was obtained in a loosely coalescent form crumbling readily on shaking and evolved heat when taken to the air. The metal (3.5 g.) contained in the reaction tube was again heated at 300–400° in the atmosphere of hydrogen, then, without entrance of air, treated in vacuum at 250°, and washed with hydrogen bromide gas. Hydrogen bromide (20 g.) and allyl bromide (24 g.) collected in the mixing tube were then distilled in vacuum into the reaction tube containing reduced nickel. The reaction tube was sealed off without entrance of air, slipped into an iron pipe, and shaken at room temperature for three days. The contents were treated as described previously.(4) The results are shown in the accompanying table (exp. 1 and exp. 2). Ninety-five per cent. of the product was 1,3-dibromopropane in both experiments. The reduced nickel appeared to have not suffered the slightest attack by hydrogen bromide and the liquid remained colourless after reaction.

In the additions in the presence of commercial reduced iron (Kahlbaum) about seventy per cent. of the product was 1,3-dibromopropane (see the tables of the first and the second papers).(1)(2) It was already anticipated that the effect of freshly reduced iron would be more conspicuous.(5) A result as

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(2) The second paper of this series, this Bulletin, **11** (1936), 754.

(3) Adsorbed or absorbed oxygen, if any, was removed by evacuating at 250° and washing with hydrogen bromide gas.

(4) For the details of the experimental procedure see the first paper.

(5) This Bulletin, **11** (1936), 756.

No. of exp.	Catalyst	Product: Dibromopropanes			
		Yield (%)	Boiling point (°C./mm.)	1,3-(%)	1,2-(%)
1	Reduced nickel free from oxides, 3.5 g.	40	44—53/11	95	5
2	Reduced nickel free from oxides, 3.5 g.	60(6)	43—54/10	95	5
3	Freshly reduced iron, 3.4 g.	40	40—53/10	92	8
4	Reduced cobalt free from oxides, 3.5 g.	30	32—46/10	38	62

shown in the table (exp. 3) has really been obtained with reduced iron prepared by freshly heating the commercial product at 300–400° in the stream of hydrogen. Reduced iron prepared in this way evolved no heat in the air. The addition was carried out in the same way as with reduced nickel, except that in this case the metal was used without treating with hydrogen in the reaction tube. The addition product was found to contain more than 90 per cent. 1,3-dibromopropane. The metal was not attacked by hydrogen bromide also in this case and the liquid remained colourless after the reaction.

On account of the fact that cobalt does not resist against the action of hydrogen bromide in allyl bromide in contrast with nickel and iron, with commercial reduced cobalt no effect, and even with freshly reduced cobalt only a small effect, on the direction of addition of hydrogen bromide to allyl bromide were observed (see the table of the second paper).(2) With reduced cobalt prepared by heating the commercial product at dull red-heat in the stream of hydrogen and freed from traces of oxides by reducing again in the reaction tube, a similar result has been obtained (exp. 4). The metal suffered seriously the attack by hydrogen bromide.

The alternating resistance of the three metals of the iron group to hydrogen bromide in allyl bromide finds its counterpart, for instance, in the alternating ease with which they form metal-carbonyls.

The results obtained with the special precaution of eliminating traces of oxides have thus established the well-defined influence of the ferro-magnetic metals on the addition of hydrogen bromide to allyl bromide. They not only inverse the proportion of the normal and the abnormal addition products, but also increase the total yield of the products. Thus the effect of the ferro-

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(6) The cause of the exceptionally good yield of exp. 2 is unknown, except that reduced nickel used in this experiment was prepared with nickel oxide from a new bottle (Kahlbaum, "cobalt free").

magnetic metals resembles the so-called peroxide effect of oxygen so far as the results of addition of hydrogen bromide to allyl bromide are concerned. It has now been made very probable that the peroxide effect of oxygen, and also even of peroxides, may be attributed to the action of oxygen itself and not of any formed peroxide.(7) Then, oxygen, the gaseous substance with the greatest magnetic susceptibility, and the ferro-magnetic metals exert similar influences on the addition of hydrogen bromide to allyl bromide. It may be assumed that these substances with great magnetic susceptibilities activate allyl bromide by changing the state of its molecule from a type suitable for the normal addition into one suitable for the abnormal addition, say by means of electron displacement, while platinum black with no significant influence on the composition, but with an increasing effect on the yield, of the product(8) seems to activate hydrogen bromide.

It is thinkable that in organic chemistry there may be not a few cases of the catalytic action by aerial oxygen which have hitherto been unnoticed. For instance, M.S. Kharasch and M. Foy(9) state that the presence of peroxides is necessary for the Cannizzaro reaction to take place, air or oxygen being also effective because of the formation of peroxides, and the heavy metal ions, which were once considered to accelerate the Cannizzaro reaction by themselves, have only a catalytic effect on the peroxide formation but no direct influence on the Cannizzaro reaction itself. But it may be more reasonable to consider that the heavy metal ions would facilitate the decomposition of peroxides, and that peroxides could not stay long in alkali so strong as used in the Cannizzaro reaction, unless very minute traces of peroxides are concerned. Thus it is possible that the active catalyst is really molecular oxygen. The decision awaits for further experimental evidence.

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(7) The third paper of this series, this Bulletin, **11** (1936), 798. P.L. Harris and J.C. Smith, *J. Chem. Soc.*, **1935**, 1572, "emphasize that in the absence of air the catalysts perbenzoic acid, benzoyl peroxide, 10,11-epoxyundecoic acid, and α-heptenylheptaldehyde have a very small influence on the composition of the product from hydrogen bromide and undecenoic acid," and point out that "at least with this olefin molecular oxygen is essential for the peroxide effect." But, that the peroxide effect is to be attributed to the catalytic action of molecular oxygen itself, neither is shown by their investigations, nor seems to be meant by their statement, because they summarize their results by saying "none of the catalysts is effective in absence of molecular oxygen," thus recognizing the necessity for the presence of molecular oxygen only in order that their "catalysts" may bring about the peroxide effect.

(8) See the table of the first paper, this Bulletin, **11** (1936), 693.

(9) *J. Am. Chem. Soc.*, **57** (1935), 1510.