On the Reaction of Gaseous Hydrogen Bromide with Reduced Nickel in the Presence of Oxygen.

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In a preliminary note⁽¹⁾ the authors reported that in the dark at room temperature hydrogen bromide reacted with reduced nickel in presence of oxygen to give nickel bromide and hydrogen, while practically no reaction took place in absence of oxygen. The experimental details are given below:

In a glass tube with a capacity of 65 c.c. 0.5 g. of reduced nickel was taken; the air in the tube evacuated; hydrogen introduced; the nickel heated at 350–360° for ten minutes; the hydrogen evacuated thoroughly at the same temperature; and the tube with the nickel cooled down. With or without admission of 10 c.c. (4.3×10^{-4} mol) of oxygen, 45 c.c. (19.2×10^{-4} mol) of hydrogen bromide was introduced, and the tube was sealed off. The tube was left to stand in the dark or in diffuse light at room temperature for 14–15 days. A capillary seal attached to the tube was thrusted into an end of a piece of rubber tubing, the other end of which was connected with a trap and a manometer. The trap was evacuated and cooled in liquid air. The capillary seal inside the rubber tubing was broken from outside, and the pressure of the incondensable gases was read when the height of mercury in the manometer reached a stationary state. From the pressure and the approximate volume of the whole system the amount of the gases was calculated, the effect of cooling the trap on the pressure being taken into account. The reduced nickel, which showed no change in appearance in every case, was extracted with 25 c.c. of warm water. Aqueous caustic potash was added to the resulting solution; nickel hydroxide precipitated was collected and dissolved in hydrochloric acid; and nickel was estimated with dimethyl-glyoxime. Bromide ion in the filtrate from nickel hydroxide was determined by Volhard's method; and the amount of hydrogen bromide which reacted was calculated from the value of bromide ion. The results are given in Table 1.

In absence of oxygen, either in the dark (Exp. 1) or in diffuse light (Exp. 2), practically no reaction took place. Owing to the great percentage of error involved in the estimations of small amounts of the in-

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(1) This Bulletin, **13** (1938), 407.

Table 1. Reduced nickel 0.5 g. Hydrogen bromide 45 c.c. (19.2×10^{-4} mol). At room temperature. Reaction time 14–15 days.

Exp. No.	Remarks	Incondensable gases (10^{-4} mol)	Found in the extract of reduced nickel			Hydrogen bromide which reacted (%)
			Ni (10^{-4} g. atom)	Br (10^{-4} g. atom)	Ni : Br	
1	No oxygen In the dark	0.4	0.9	2.0	1 : 2.2	10
2	No oxygen In diffuse light	0.5	0.8	2.3	1 : 2.9	12
3	Oxygen 10 c.c. (4.3×10^{-4} mol). In the dark	11	7.8	16.4	1 : 2.1	85

condensable gases and nickel bromide, the numerical values obtained in Exps. 1 and 2 are not exact.

In presence of oxygen as much as 85 per cent of hydrogen bromide introduced reacted (Exp. 3). If first reduced nickel were oxidized by oxygen and then hydrogen bromide reacted only with nickel oxide thus formed to give nickel bromide and water, nearly no incondensable gases would be left after 16.4×10^{-4} mol of hydrogen bromide reacted with nickel in presence of 4.3×10^{-4} mol of oxygen. On the other hand, if all hydrogen of the hydrogen bromide which reacted were converted into molecular hydrogen, the total amount of oxygen and hydrogen would be 12.5×10^{-4} mol. In fact, the amount of the incondensable gases was found to be 11×10^{-4} mol after reaction.

Thus, the authors drew the conclusion that in presence of oxygen hydrogen bromide reacted with reduced nickel to give nickel bromide and hydrogen without the formation of water, and then supposed the activation of hydrogen bromide by oxygen in this reaction. Such a hypothesis seemed not unreasonable in view of the following facts: Oxygen activates hydrogen bromide to isomerize isostilbene to stilbene(2) and affects the addition of hydrogen bromide to unsaturated organic compounds(3); and, although reduced nickel shares such a property with oxygen,(2)(4) it does not react with hydrogen bromide in absence of oxygen.

However, another possibility was that, if even a trace of water were produced by the oxidation of reduced nickel followed by the reaction of nickel oxide thus formed with hydrogen bromide, that trace of water might

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(2) This Bulletin, **12** (1937), 507; **13** (1938), 566.

(3) *Ibid.*, **11** (1936 , 692, 798; **12** (1937), 138, 173; **13** (1938), 331.

(4) *Ibid.*, **11** (1936), 692, 754; **12** (1937), 51; **13** (1938), 331, 400.

accelerate the reaction of hydrogen bromide with reduced nickel giving nickel bromide and hydrogen. Thus it seemed desirable to study the effect of water on the reaction of hydrogen bromide with reduced nickel and further to analyse the incondensable gases obtained in the reaction in presence of oxygen to know exactly the amount of hydrogen generated.

Table 2. Reduced nickel 0.5 g. Hydrogen bromide 45 c.c. (18.5×10^{-4} mol). At room temperature. In the dark. Reaction time 14–15 days.

Exp. No.	Added	Hydrogen produced (10^{-4} mol)	Found in the extract of reduced nickel			Hydrogen bromide which reacted (%)
			Ni (10^{-4} g. atom)	Br (10^{-4} g. atom)	Ni : Br	
4	Oxygen 10 c.c. (4.1×10^{-4} mol)	4.7	7.8	15.9	1 : 2.0	86
5	None, but reduced nickel exposed to air before use	4.3	6.4	12.2	1 : 1.9	66
6	Water 3 mg. (1.7×10^{-4} mol)	4.5	4.6	9.6	1 : 2.1	52
7	Water 3 mg. (1.7×10^{-4} mol)	5.4	5.5	11.5	1 : 2.1	62
8	None	0.6	0.9	2.2	1 : 2.4	12

In Table 2 another series of experiments carried out for this purpose are summarized. The procedure and the conditions of the experiments were the same as mentioned above unless otherwise stated below. To analyse the incondensable gases, oxygen was absorbed in alkaline pyrogallol and hydrogen was determined by the explosion method. The incondensable gases obtained in Exp. 4 was found to consist of 3.7×10^{-4} mol oxygen and 4.7×10^{-4} mol hydrogen. The percentage of hydrogen bromide which reacted was the same as in Exp. 3. The amount of hydrogen produced was found to be smaller than equivalent to that of nickel bromide formed.

In Exp. 5 reduced nickel was exposed to air before use, but treated in vacuum at room temperature before the introduction of hydrogen bromide; and the reaction took place without added oxygen. It was shown that the reaction of hydrogen bromide with reduced nickel was caused by combined or adsorbed oxygen on the reduced nickel. In the gas analysis no oxygen was detected and the amount of hydrogen was found smaller than equivalent to that of nickel bromide also in this case.

In Exps. 6 and 7, a trace of water (3 mg. or 1.7×10^{-4} mol) was added as follows: A tube containing 6 mg. of Glauber's salt was connected with the reaction tube through a cock. The Glauber salt tube was cooled in liquid air, evacuated, filled with hydrogen, again evacuated, and the cock was closed. Reduced nickel in the reaction tube was treated as previously mentioned; the water of crystallization was vapourized into the reaction tube by opening the cock and heating the Glauber salt; the cock was closed again; and hydrogen bromide was introduced into the reaction tube. In this way, it was found that hydrogen bromide reacted with reduced nickel in presence of water but in absence of oxygen. Hydrogen was of course the only incondensable gas and its amount was equivalent to that of nickel bromide formed.

Thus, for the reaction of gaseous hydrogen bromide with reduced nickel in the presence of oxygen, although no evidence has been obtained to deny that oxygen may act also as a catalyst, it is the most probable that the reaction of hydrogen bromide with reduced nickel to give nickel bromide and hydrogen is accelerated by a trace of water supplied by the oxidation of reduced nickel followed by the action of hydrogen bromide on the oxide formed. The alternative, but less probable, mechanism of the formation of water may be the catalytic oxidation of hydrogen bromide by oxygen in presence of reduced nickel, freed bromine combining with reduced nickel.

To consider the matter more closely, adsorption should be taken into account. However, it is beyond the scope of the present study, which has been schemed with a view to obtaining grounds for explaining the effects of oxygen and of ferromagnetic metals on the addition of hydrogen bromide to unsaturated organic compounds(3)(4) and on the isomerization of isostilbene to stilbene by hydrogen bromide,(2) and which has resulted in finding, perhaps, a combined case of the attack by a hydrogen halide on a metal preceded by the oxidation by oxygen and the activation of a hydrogen halide by a trace of water.

A reaction which seems to be of a similar type was reported by G. H. Bailey and G. J. Fowler,(5) who found that, when hydrogen bromide and oxygen were kept on mercury in the dark, hydrogen was produced together with water.

Further, the present authors observed reactions of different types with platinum black and with reduced copper: While platinum black and hydrogen bromide did not react in absence of oxygen, they gave in presence of oxygen a small amount (6 mg. from 0.2 g. platinum black, 45 c.c. hydrogen bromide and 10 c.c. oxygen in 17 days) of a substance which

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(5) *J. Chem. Soc.*, **53** (1888), 755.

was not examined closely but was undoubtedly bromoplatinic acid, neither free bromine nor hydrogen being detected. Reduced copper and hydrogen bromide reacted nearly to the exhaustion of the latter either in presence or in absence of oxygen, cuprous bromide being formed in either case.

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