

XXIII.—*Investigations into the Action of Substances in the Nascent and Occluded Conditions. Hydrogen (continued).*

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FROM our recent study of the behaviour of nascent and occluded hydrogen (*Chem. Soc. Trans.*, 1878, 306) we arrived at the opinion that these hitherto supposed different states of the element are very closely related, if not identical—that, in fact, the activity of the so-called nascent hydrogen is only the consequence of its intimate association with the metals employed to bring about the liberation of the element.

To test this conclusion still further, we determined to examine the action of nascent and occluded hydrogen on other bodies. The two acids, nitric and sulphuric, presented themselves to our mind more especially, because the results, whether they strengthened our hypothesis or not, would certainly assist in the elucidation of the chemistry of the action of metals upon these compounds.

Nascent Hydrogen and Nitric Acid.

The usual way of preparing nascent hydrogen is by acting on a metal by means of an acid, and the first idea might be that the action of nitric acid on zinc or some other metal would itself furnish the body upon which we intended to experiment. But a moment's reflection will show that the nitric acid in attacking a metal can only generate hydrogen by becoming itself a nitrate, and thus introducing a third body into the reaction, while every chemist knows that the nitric acid itself is actually more or less deoxidised; and how far this is dependent on, or independent of, nascent hydrogen, it is impossible to say. There seemed, in fact, to be only one source of hydrogen which was unexceptionable, that from the electrolysis of the acid itself. This electrolytic hydrogen is pre-eminently in a nascent condition, and it does not matter for our purpose whether we suppose that is the HNO_3 or the accompanying H_2O that primarily suffers decomposition.

We are not without former experiments on this subject. Faraday (*Phil. Trans.*, 1834) taught that in the electrolysis of very strong nitric acid no free hydrogen appeared at the cathode, but nitrous acid, and apparently, after some time, nitric oxide; further, that when the strong acid was mixed with an equal or greater bulk of water, hydrogen alone appeared, varying in quantity with the strength of the

acid or voltaic current, but equivalent to the oxygen at the anode. Bourgoin (*J. Pharm.* [4], 13, 266—270), who has more recently (1871) investigated this subject, finds, like Faraday, that the strongest acid gives no free hydrogen at the cathode, but that hydrogen alone appears there only when very dilute acid is employed. When acids of the strengths 5.2 and 14.6 per cent. respectively were used, hydrogen only was set free at the beginning of the action; nitrogen subsequently made its appearance, and also ammonia, but these substances are most probably not produced by the action of hydrogen on nitric acid, but are secondary or tertiary products of this action.

It would appear, then, that electrolytic or so-called nascent hydrogen reduces strong nitric acid, but only imperfectly, or not at all, when diluted with an equal bulk or more of water. But if the oxidation of the freed hydrogen in this action results from its being in the occluded condition, the reduction of the acid would depend upon the strength only in so far as this facilitated the de-occlusion of the hydrogenised electrode, and the stronger acid might be expected to do this the more readily. And it follows that with a given strength of acid, the amount of free gaseous hydrogen should bear some relation to the rate at which the electrolysis takes place: for were the gas freed from its nitric radicle more slowly, or not faster than it could pass into the occluded condition, none should bubble through the liquid; but were the rate of production of the element greater than that at which it is absorbed by the platinum electrode, some should escape, the quantity depending on the excess of the former over the latter action. This view offers a satisfactory explanation of the general results so far as they go, obtained by both Faraday and Bourgoin, and our own experiments on the electrolysis of the acid still further increase its probability.

The apparatus used by us was Hofmann's arrangement for illustrating the composition of water electrolytically. Each experiment went on until the same quantity (35 c.c.) of oxygen collected at the anode. The results, with other particulars, are given in the annexed table (p. 174).

It may be observed that no free hydrogen was liberated in any of the experiments with the 68 per cent. acid, nor in the first with the 1 : 1 acid; but in the second experiment with this strength, where the rate of decomposition was five times greater than in the first, some was set free; in the third, where the decomposition proceeded still more rapidly, more; and in the fourth, where again it was faster, still more gas escaped oxidation. The same general result is obtained with the weakest acid, but the proportion of free hydrogen for a given battery power is much greater. Our explanation is, that in all the experiments of the first series, as in the first of the second, the hydro-

Grove's cells employed.	Strength of nitric acid.	Time of experiment.	Negative pole.		
			Reduction in c.c. of oxygen.*	Free hydrogen.	H equal to NH ₃ found.
1	1 68·2 p.c.	3 hours	31·5	Nil	Nil
2			28·4	"	"
4			22 "	"	"
8			29·4	"	"
1	1 : 1	3 hrs. 35 mins.	30·6	Nil	Nil
2		42 mins.	29	2 c.c.	"
4		19 "	24·2	9 "	"
8		8 "	16·8	22 "	Trace
2	1 : 2	61 mins.	17	30 c.c.	2 c.c.
4		18 "	0·5	65·7	Nil
8		8 "	0·3	68·7	"

gen was occluded at least as fast as produced—in fact, it is probable that at no moment in any of these trials was the platinum electrode fully charged with hydrogen: but that in the second experiment of the second series the gas was produced a little more rapidly than it was absorbed and oxidised; in the third experiment more, and in the fourth still more; whilst in the third series the same relation obtains, but the weaker acid being less readily deoxidated by occluded hydrogen, a greater quantity of the gas escaped through the liquid than in the corresponding trials with the stronger acid.

There is one very curious feature of this action to which we would now direct attention. In the second, third, and fourth experiments with the 1 : 1 acid, the evolution of hydrogen gas at the cathode ceased almost entirely and quite suddenly in three minutes, and in the first experiment with the 1 : 2 acid in 40 minutes. This evolution of hydrogen at the beginning only of the electrolysis of nitric acid was noticed by Bourgoin, and some long time previously by Schönbein. The first of these investigators made no attempt to account for the fact, while the latter attributed it to some *peculiar* condition into which the platinum electrode becomes thrown. We, on the contrary, have traced it to the presence of nitrous acid, which we find almost entirely prevents the escape of hydrogen with a battery power of 8 cells, when present in the proportion of 0·059 gram to 100 c.c. of the 1 : 1 acid.

The study of the action of the copper-zinc couple on aqueous nitre

* Determined by permanganate of potassium.

solution taught us that nitrite and nitrate of potassium suffer, when in admixture, simultaneous decomposition, and it would appear that the same obtains with their hydrogen analogues; and, moreover, that the mixture oxidises hydrogen more readily than does nitric acid alone.

Occluded Hydrogen and Nitric Acid.

Nothing is known, so far as we are aware, regarding the action of occluded hydrogen on nitric acid, but Dr. Armstrong (*Chem. Soc. J.*, 1877, 2, 82) found hydrogen in the gaseous products of the action of nitric acid on a sample of nickel which Dr. Russell had prepared by reducing its oxide in a current of the gas, and inferred that it was hydrogen which had been occluded, and therefore escaped oxidation. He suggested this also as a means of investigating hydrogen-palladium.

The metal platinum, as is well known, is not attacked by nitric acid, and readily occludes hydrogen. For these reasons the gas was associated with this metal in order to study its action on nitric acid. A quantity of the metal was obtained in the most favourable form by precipitation with an alkaline formate. To ensure freedom from possible reducing matter, after being thoroughly washed and dried, it was boiled with strong nitric acid, again washed, and once more dried with as little contact with the air as possible. Nitric acid was not in the least acted upon by the metal thus prepared. The pure finely divided platinum was then charged with hydrogen by heating to 100° C. and cooling in that gas.

In a preliminary experiment, it was found that on dropping some pure nitric acid (68 per cent.) on to about 30 grams of the elements, a violent action was at once set up, the heat produced being sufficient to render the metal red hot, and to make us greatly fear an explosion, which convinced us that occluded hydrogen has, in this combination at least, a very decided action on nitric acid. A quantitative experiment was made by pouring very quickly 40 c.c. of the same colourless acid on 20 grams of the hydrogenised metal, when signs of reduction were almost at once noticeable by the yellow colour of the liquid and the escape of a small quantity of nitrous fumes. In 15 minutes the liquid reduced a quantity of potassium permanganate corresponding with 0.0372 of nitrous acid, and contained 0.0025 gram of ammonia. In another similar trial but with 1 : 1 acid, the reduction in 15 minutes corresponded with only 0.015 gram of nitrous acid, and 0.0016 gram of ammonia, showing still further the analogy between the action of electrolytic and occluded hydrogen on nitric acid.

But although the fact is thus satisfactorily established that hydrogen, when associated with a metal not acted upon by nitric acid, may be readily oxidised by it, such might not be the case were the gas

associated with a metal that is itself acted upon by the acid. Now, palladium both occludes hydrogen and is acted upon by nitric acid, especially when the latter contains nitrous acid, and therefore we thought an experiment with palladium-hydrogen and nitric acid might give results of some interest in settling this point. 2.5 grams of palladium were associated with about 120 c.c. of hydrogen, and some 18 c.c. of 1 : 1 acid quickly poured on. The metal slowly but completely dissolved without a trace of gas being set free, from which it would appear that whether the hydrogen be associated with a metal itself acted upon or not, it is still readily oxidised by nitric acid.

Nascent Hydrogen and Sulphuric Acid.

Again, the only source of nascent hydrogen available is that from the electrolysis of the acid. Faraday, who investigated this action also in 1834, found that oxygen separated at the anode, and sulphur and pure hydrogen at the cathode (*Phil. Trans.*, 1834).

On studying this subject in the Hofmann's apparatus mentioned above, with pure redistilled oil of vitriol containing 98.2 per cent. H_2SO_4 , and variable battery power, results were obtained agreeing with Faraday's. We observed, moreover, that immediately the action was started with two or more cells, the sulphur formed a film over the negative electrode, which increased but only with comparative slowness during the continuance of the experiment. This is significant, and no doubt has a very considerable influence on the relative proportions of the two elements set free, and very probably accounts for the appearance of free hydrogen at all, at least where the smaller battery power was employed: for this film must necessarily retard the occlusion of the freed hydrogen, and, therefore, according to our view, compel the greater part of the gas to escape out of the liquid. Evidence of the correctness of this reasoning was given by very carefully noting the amounts of gas set free in the first minute or two of the action, starting first with a clean and afterwards a sulphur-covered plate. With the latter a greater quantity of hydrogen always escaped for an equal amount of gas collected at the anode.

An idea of the amount of gas which escapes with different battery power, may be gathered by glancing at the annexed table. In each case the electrolysis went on until 11.5 c.c. of gas (oxygen, but with some ozone) had collected at the anode:—

Battery power.	Time.	Hydrogen.
2	3.5 hours	18 c.c.
4	1 hour	23 "
8	23 mins.	26 "

It might be expected that hydrogen acting on sulphuric acid would set free sulphurous anhydride thus :—



We could not, however, detect this substance in any of the experiments just detailed. But the reason of this, we thought, might be found in the quantity of the occluded gas being at any moment of the experiments sufficient to combine, apparently in one operation, with the three available atoms of oxygen in the acid molecule; and that if the gas were presented much more slowly, evidence of this very natural chemical change would be forthcoming. An experiment was therefore started with one cell. The amount of action was exceedingly small, only about one and a half c.c. of gas being collected at the anode in ten days. At the cathode not a trace of gas or sulphur appeared, but the liquid there was found to contain an appreciable amount of sulphurous anhydride.

It appears, then, that hydrogen, when associated with platinum, reduces oil of vitriol very readily, and that when the gaseous element is present in very small quantity, sulphurous anhydride is one of the products. The appearance of sulphur on the metallic electrode always results, very probably, from the complete deoxidation of this latter compound, which is much facilitated, no doubt, by the viscosity of the medium in which it is produced. Proof that occluded hydrogen does really bring about this reduction of sulphuric acid we now give.

Occluded Hydrogen and Sulphuric Acid.

Palladium Hydrogen.—The metal was obtained in a finely divided condition, and hydrogenised in the usual manner. On heating for one hour at 100° in a current of carbonic anhydride, as described below, 5 grams of the non-hydrogenised metal with 10 c.c. of the 98.2 per cent. acid, little or no sulphurous anhydride was evolved; but on pouring a few c.c. of the acid on a little of the metal charged with hydrogen, the odour of the sulphurous gas was immediately noticeable. The fact that sulphurous anhydride is abundantly evolved under these circumstances was completely established by quantitative trials, particulars of some of which we subjoin.

Experiment A. 10 c.c. of the acid were poured on 5 grams of the hydrogen-palladium. The sulphurous anhydride as produced was driven from the acid which absorbs it, by bubbling carbonic anhydride through the liquid. This was continued for 40 minutes at the ordinary temperature, and five minutes at about 100° . The amount of sulphurous gas which formed was found by iodine solution to be 0.592 gram.

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Experiment B. Similar to A. The sulphurous anhydride was, however, estimated at intervals, when it was found that—

0·457 gram formed in the first 30 minutes, at the ordinary temperature.

0·152 gram formed in the next 30 minutes at 100°, and

0·001 gram formed in the next 30 minutes at 100°,

making a total in the hour and half of 0·61 gram.

Experiment C. Used 20 c.c. of the acid. In all other particulars the same as B. The amount of sulphurous anhydride formed was—

0·344 gram in the first 30 minutes, at the ordinary temperature,

0·261 gram in the next 30 minutes at 100°, and

0·016 gram in the next 30 minutes, at 100°,

making a total of 0·621 gram.

Oil of vitriol, then, not only very readily oxidises occluded hydrogen, but, it would appear, from the amounts of sulphurous anhydride produced in the several experiments being almost identical, that a definite proportion of the gas (some 72·4 per cent.) when associated with palladium, suffers this change.

Hydrogen-palladium has also a very slight reducing action on sulphuric acid mixed with an equal bulk of water.

Hydrogen Platinum.—Hydrogen associated with finely divided platinum prepared as already described, reduces oil of vitriol to sulphurous anhydride, but much less energetically than palladium-hydrogen.

Two views appear to be held with regard to the formation of the reduction-products in the action of metals on nitric acid and oil of vitriol: one that they result from the direct reducing action of the metallic elements; the other, that the reductions are effected by nascent hydrogen produced by the initial action of the metals on the respective acids. These views are alike, in so far that both are based upon analogical rather than on experimental evidence. The first derives support from the fact that certain non-metallic elements are oxidated by the bodies in question; and the second, from the general behaviour of metals with the class of compounds designated acids.

Reasoning on the lines of this research, we saw that direct proof of the truth of the second, and more probable view, might not be impossible to find. Now, in order to obtain the evidence of the liberation of hydrogen which this view requires, it appeared only necessary to bring about the initial action at such a rate, that the liberation of the gas should be faster than it could pass to the occluded condition. And to ensure the greatest probability of doing this, it further appeared necessary to employ, firstly, the metal of maximum available activity, and, secondly, a large volume of acid relatively to the metal, in order to minimise the influence of reduction-products. Magnesium was natu-

rally suggested. In each of our experiments a piece of this metal in thin sheet ($1 \times \frac{5}{8}$ -inch), weighing 0.4 gram, was placed in the centre of 350 c.c. of the nitric acid liquid.

Experiment I. Used 68 per cent. acid. The metal became coated at once with a whitish powder, and very slowly dissolved, with evolution of a minute quantity of gas, the liquid, as the action proceeded, acquiring a yellow colour. In 54 minutes the metal remaining undissolved suddenly decomposed the acid, with almost explosive violence. The total gas collected measured only 3 c.c. It was neither combustible nor explosive.

Experiment II. Used 1 : 1 acid. The metal did not tarnish, but entirely dissolved in 1—2 seconds, with evolution of gas, the first 3 c.c. of which burnt almost noiselessly; the second 3 c.c. detonated slightly; and the next 6 c.c. burnt still more explosively.

Experiment III. Used 1 : 2 acid. The general result was the same as in II. A little more gas was evolved, and the first 3 c.c. burnt somewhat less noiselessly than the corresponding portion in II. Further evidence of the production of hydrogen appeared unnecessary.

Among other results of this investigation, then, we may claim to have demonstrated the possibility of the replacement of hydrogen in nitric acid by a metal, a fact which very greatly supports, and removes from the region of conjecture, the view which regards the reduction-products already referred to, as formed by the direct action of hydrogen. We may also claim to have established still more fully the close likeness of character, and therefore of condition, between hydrogen usually denominated *nascent*, and hydrogen occluded by metals.
