a three-hour exposure the bands were too weak to permit exact measurements and all attempts to increase the intensity failed. It was found that the solid acetaldehyde condensed in the trap also glowed under the influence of the active gas, the color being about the same as that given by acetaldehyde in the vapor state.

Summary

The action of atomic hydrogen prepared by Wood's method on some solid and gaseous organic compounds has been studied. It has been found that atomic hydrogen for the most part acts as a rather mild reducing agent, reducing azoxybenzene at least partially to azobenzene and azobenzene partially to hydrazobenzene with aniline as the final product. Certain solid dyes are reduced to colorless compounds which are partially reoxidized to the colored form on exposure to air. Benzoic acid and acetamide catalyze the recombination but are not noticeably reduced.

Atomic hydrogen recombines in the presence of formic acid. A small amount of formaldehyde is produced, probably due to the decomposition of the acid by heat into water and carbon monoxide and the subsequent formation of the aldehyde from carbon monoxide and atomic hydrogen. Acetaldehyde is polymerized to paraldehyde. A faint blue chemiluminescence was observed.

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[Contribution from the Chemical Laboratory of The Johns Hopkins University]

REACTIONS OF DISSOCIATED WATER VAPOR

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It is well known that if an electric charge is passed through water vapor at low pressures the Balmer series of hydrogen and the so-called water bands appear with great intensity. Thus it appears that water is dissociated into H and OH in the electric discharge. Also the fact that the OH bands are emitted[1] by the gases leaving Wood's tube as used in the production of atomic hydrogen shows that the OH molecule can be pumped to considerable distances from the discharge tube. It was thought worth while to see whether atomic hydrogen and OH molecules formed by the dissociation of water vapor in an electric discharge could be detected outside the tube.

Experimental

The only change in the atomic hydrogen apparatus described in the preceding paper was the substitution of a flask of water for the tank

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[1] See Bonhoeffer, *Z. physik. Chem.*, **116**, 391 (1925).

of hydrogen and the bubbler C. The oil pump was of the type which permitted the collection of gases coming from the apparatus. An analysis showed that more than two-thirds of the gases leaving the apparatus was hydrogen. Two typical analyses are given below. In the last column is given the excess of hydrogen over that necessary to react with the oxygen to form water.

Total quantity of gas, cc.	O_2, cc.	H_2, cc.	Excess H_2, %
21.50	5.90	15.10	21.85
21.80	6.20	15.60	20.51

Hydrogen peroxide was detected in the water condensed in the trap, which seems to account for the excess hydrogen in the gaseous products. These results are in accord with some old observations of Thompson, who showed that if water vapor is decomposed by an electric spark, an excess of hydrogen over that necessary to react with the oxygen to form water is obtained, and also with those of Kernbaum,[2] who passed a brush discharge through water vapor and found that hydrogen peroxide was formed.

The gases leaving the discharge tube were found to be very active. A strip of platinum exposed to these gases glowed with greater intensity than when exposed to atomic hydrogen produced in the same tube. It was heated almost white hot. From the considerations mentioned in the introduction it seems probable that atomic hydrogen and OH molecules are both present in these gases. The following experiments were carried out to prove the existence of these two constituents.

Evidence for the Presence of Atomic Hydrogen.—Langmuir,[3] Cario and Franck,[4] and Bonhoeffer[5] have shown that atomic hydrogen will reduce copper oxide at room temperatures. A piece of copper gauze was oxidized in the Bunsen flame, part of the gauze being left unoxidized in order to determine whether the active gas was oxidizing or reducing. The gauze was placed in the bottom of a trap, H, as shown in Fig. 1 of the preceding paper, which was about 25 cm. from the discharge tube. The copper oxide was reduced to bright metallic copper and the bottom of the trap became quite warm during the reaction. Evidently the gases are reducing rather than oxidizing in character. A crystal of copper sulfate placed in the apparatus was immediately reduced to the metal. At the beginning of the reaction the crystal appeared to be black, indicating that the salt was probably decomposed into copper oxide and some other product before final reduction took place. The copper was smooth,

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[2] Kernbaum, *Compt. rend.*, **151**, 319 (1910).

[3] Langmuir, THIS JOURNAL, **44**, 860 (1922).

[4] Cario and Franck, *Z. Physik*, **11**, 161 (1922).

[5] Bonhoeffer, *Z. physik. Chem.*, **113**, 199 (1924).

giving the impression of having been fused. The water condensed in another trap which was surrounded by liquid air gave a test for sulfate. Indigo was exposed to these active gases and as in the case when it is exposed to atomic hydrogen it was reduced to indigo white. Small portions of the solid indigo were torn off and became incandescent. No such violent action was observed in the experiments with atomic hydrogen described in the preceding paper.

The chemiluminescence observed when acetaldehyde was exposed to the action of atomic hydrogen[6] was also observed when acetaldehyde was exposed to these gases. Moreover, mercury exposed to the action of these gases emitted a visible violet light which consisted of the HgH bands and also the 2536 Å. line of mercury. The mercury was placed in the bottom of the trap used to study the reduction of copper oxide; a beaker containing water at about 50° was placed around the trap. As the mercury warmed up the luminous region separated into two parts, one of which traveled slowly up the walls of the trap and the color changed from violet to green. The separation is due to the fact that distillation took place and the mercury condensed in the upper, cooler portions of the trap. As Bonhoeffer has shown,[5] mercury is excited by atomic hydrogen only in the neighborhood of liquid mercury. Thus the separation of the luminous region into two parts is explained. The interesting point in this observation is that atomic hydrogen must have passed through a region containing mercury vapor without exciting the mercury vapor to emit light and without being destroyed by recombination to molecular hydrogen. A quartz window was attached to the side of the trap and a photograph taken with the small Hilger quartz spectrograph. The mercury hydride bands were obtained along with the 2536 Å. line of mercury. All these observations have been made previously when atomic hydrogen alone is present in the exit gases.

Experiments Indicating the Presence of the OH Molecule.—The gas coming from a water discharge tube seems to be even more active than atomic hydrogen. Bonhoeffer was unable to effect the reduction of nickel chloride and iron chloride with atomic hydrogen, but these two salts are reduced to the metal by the gases leaving the water discharge tube.

Olson and Meyers[7] have found that ethylene reacts with atomic hydrogen to form methane, ethane, propane and butane. This suggests that OH molecules might react with ethylene to give an addition product containing oxygen, as, for example, ethyl alcohol or glycocoll. The ethylene was allowed to mix with the active gases coming from the discharge tube and any products resulting were collected in a trap cooled

[6] Urey and Lavin, THIS JOURNAL, 51, 3286 (1929).

[7] Olson and Meyers, *ibid.*, **49**, 3131 (1927).

with liquid air. Blank tests were first run, without passing the discharge through the streaming water vapor. The liquids caught in the trap did not give the iodoform test for alcohol nor did they reduce Fehling's solution. The discharge was then turned on and a similar experiment made.[8] No back diffusion of the ethylene gas took place, for otherwise there would have been a change in the spectrum of the discharge tube, which was not observed. Moreover, simple calculations showed that with the approximately known velocity of the water vapor leaving the discharge tube such back diffusion could not have taken place. The liquid which condensed in the trap had the odor of acetaldehyde, gave the iodoform test and reduced Fehling's solution. This seemed to indicate the presence of acetaldehyde. With the amounts which we were able to secure it was impossible definitely to identify any ethyl alcohol or glycocoll in the reaction products. The presence of the acetaldehyde indicates, however, that some active molecule containing oxygen must be present in the outlet gases.

An attempt was made to prove the presence of OH by taking the absorption spectrum of the gas coming from the discharge tube. No absorption coming from the known band at 3064 Å. was observed. This may not prove the absence of the OH molecule but it does seem to indicate that it must be present in rather small amounts.

Several unsaturated oils such as cottonseed oil, linseed oil, etc., were exposed to the action of the dissociated water vapor. In every case a white solid insoluble in the common organic solvents was obtained. A report of this work will appear in a forthcoming publication.

The authors are indebted to Dr. E. E. Reid for valuable suggestions and criticisms.

Summary

1. Water vapor, dissociated in a discharge tube, gives reactions which are characteristic of atomic hydrogen. From these results we conclude that atomic hydrogen is present in the active gas.

2. Water vapor seems to be more active than atomic hydrogen, in that it will reduce metallic salts which are not reduced with atomic hydrogen.

3. Active gas is prepared from water vapor with greater ease than from hydrogen.

4. It has been indicated that there is another active constituent, probably the OH molecule, present in the active gas.

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[8] The tube where the ethylene entered the apparatus became very warm during the run.