[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

SOME REACTIONS OF ATOMIC HYDROGEN

BY H. C. UREY AND G. I. LAVIN[1]

RECEIVED JUNE 22, 1929 PUBLISHED NOVEMBER 8, 1929

The preparation and properties of atomic hydrogen have been described by a number of investigators.[2] Langmuir[3] has shown that tungsten filaments at high temperatures cause the dissociation of molecular hydrogen and has used this method to study the reactions of the atomic species with various solids. Wood[4] while working on the Balmer series of the hydrogen spectrum, obtained by passing a high tension electric discharge through moist hydrogen at low pressures, showed that it was possible to remove hydrogen atoms from the discharge tube. He also pointed out that if atomic hydrogen is to be obtained from the tube the hydrogen must be moist; he assumed that the moisture poisoned the walls, thus preventing the catalytic recombination of the hydrogen atoms. Cario and Franck[5] found that hydrogen atoms are formed when a mixture of molecular hydrogen and mercury vapor is illuminated with light of wave length 2536.7 Å., the resonance line of mercury, and Taylor[6] gives an account of an improved method of using the Cario and Franck method. Bonhoeffer[7] using Wood's method has shown that atomic hydrogen reduces a wide variety of metallic oxides and salts and Boehm and Bonhoeffer[8] found that atomic hydrogen reacts with several gases. The reaction of atomic hydrogen with organic compounds has been investigated by Marshall,[9] who was unable to find any reaction between methane and atomic hydrogen. Taylor and Marshall[10] found that atomic hydrogen would react with ethylene to give ethane, and Bates and Taylor[11] found that ethylene probably reacts with atomic hydrogen to give ethyl, C_2H_5, and that there was a marked tendency for higher hydrocarbons to be formed. Recently Wartenberg and Schultze[12] have studied the action of atomic

---

[1] This paper and the following are extracts from a dissertation presented by G. I. Lavin to the Faculty of the Graduate School of Johns Hopkins University in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] See Bonhoeffer, "Ergebnisse der Exakte Naturwissenschaften," **1927**, p. 201, for a complete review to that date.

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

[4] Wood, *Proc. Roy. Soc. London*, **97**, 455 (1920); *ibid.*, **102**, 1 (1923); *Phil. Mag.*, **42**, 729 (1921); *ibid.*, **44**, 538 (1922).

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

[6] Taylor, THIS JOURNAL, **48**, 2840 (1926).

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

[8] Boehm and Bonhoeffer, *ibid.*, **119**, 385 (1926).

[9] Marshall, *J. Phys. Chem.*, **30**, 1634 (1926).

[10] Taylor and Marshall, *ibid.*, **29**, 1140 (1925).

[11] Bates and Taylor, THIS JOURNAL, **49**, 2438 (1927).

[12] Wartenberg and Schultze, *Z. physik. Chem.*, **2**, 1 (1929).

hydrogen on methane, ethane, ethylene and acetylene, and have found no reaction with methane, a catalytic recombination of the atomic hydrogen with ethane and acetylene, and a reaction of atomic hydrogen with ethylene to give ethane. Taylor and his collaborators,[13] have found that other products than ethane are produced if a large excess of hydrogen is not present. The purpose of this investigation was to try the effect of atomic hydrogen on several organic compounds in the solid and gaseous states. Since Wood's method gives atomic hydrogen in the largest amounts, this method was used in its preparation. Also, since water vapor seems to play an important role in the production or the preservation of atomic hydrogen, we have made some preliminary experiments on the active gases coming from a Wood's discharge tube when only water vapor is passed through it. The results of these experiments will be described in the following paper.

Experimental

Figure 1 represents diagrammatically the apparatus used in the work with atomic hydrogen on solid organic compounds. Hydrogen from a tank was led through a cotton wool filter, B, through a water bubbler, C and then to a system of capillaries, D. The T-tube, A, maintained a constant pressure on the incoming gases. The stopcock to which the capillaries were attached was so constructed that connection could be made to any one of the four capillaries or so that the system could be cut off entirely from the supply of hydrogen. The rate of flow of hydrogen through the capillaries with one atmosphere of pressure on one side and a few mm. on the other was 12, 22, 40 and 60 cc. per minute of hydrogen measured at atmospheric pressure. From the capillaries the hydrogen passed to the discharge tube, E, which was about a meter in length with the inlet and outlet about 25 cm. apart, and cooled by a water-bath through which water circulated continually. A trap H protected the pumps from water vapor and also served to condense any volatile reaction products. The large stopcock I was used to cut off the apparatus from the pumps. The pumping system consisted of a three-stage Gaede all steel mercury vapor pump, backed up by a large capacity oil pump; with this arrangement it was possible to pump 60 cc. of hydrogen per minute through the apparatus and still maintain a pressure of about a half mm. of mercury. The pressure in the discharge tube was measured by a McLeod gage connected at a point between the capillaries and the discharge tube. The substances to be exposed to the active hydrogen were placed in the apparatus through the ground glass joint, F. A 2 KVA transformer was

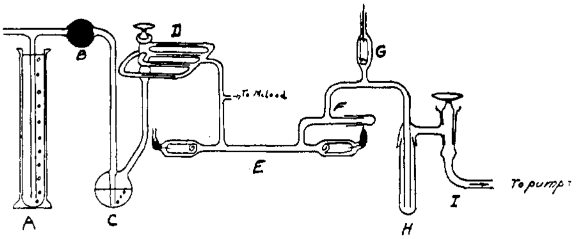

Fig. 1.

---

[13] Taylor and co-workers, *Z. physik. Chem.*, **2**, 449 (1929).

used to excite the discharge. The auxiliary electrode, G, described by Bonhoeffer[7] was used to clean out the exit tube.

It is well known that active spots may develop on the walls, causing the recombination of the atomic hydrogen, and it was, therefore, necessary to prove the presence of atomic hydrogen at the point where the solid substances were to be placed. This was done before every run by placing a small piece of platinum wire beyond this point, and being certain that the platinum was heated to a red heat before introducing the substances to be investigated. The wire was removed before the substances were introduced.

Reactions with Solid Organic Compounds.—Azoxybenzene was first exposed to the action of the atomic hydrogen; a reduction of the azoxy group to the azo group would be accompanied by a color change from yellow to red, and so would be easy to detect. Azoxybenzene was placed in a porcelain boat about 20 cm. from the discharge tube. When the discharge was turned on there was an immediate change from the yellow azoxy- to the red azobenzene. This change was accompanied by a bubbling and melting of the red mass, and aniline was detected in the trap. Azobenzene was next used and became white, indicating the reduction to hydrazobenzene. Thus we probably have the reduction Azoxybenzene ⟶ Azobenzene ⟶ Hydrazobenzene ⟶ Aniline.

Copaux, Perepot and Hocart[14] have shown that atomic hydrogen will decolorize such dyes as Indigo, Orange II and Safarine T and that the color is partially restored by exposure to atmospheric oxygen. Orange II, Pontamine Diazo Black, Auramine O[15] and Indigo were exposed to the action of atomic hydrogen. The method used in exposing the dyes was to make a paste with a few drops of distilled water; this paste was placed on small glass plates and allowed to dry. The dye-covered plates were then placed in the apparatus (about 20 cm. from the discharge tube) through the ground-glass joint, F (Fig. 1). In every case the dyes immediately turned white. When the white substances were taken from the apparatus and allowed to stand in the air some of the color reappeared, showing that the dyes had been reduced to a stage from which reoxidation to the colored compound could take place and that they had not been entirely destroyed by the reaction with atomic hydrogen. Indigo was immediately reduced to indigo white by the atomic hydrogen. That the white substance formed was indigo white was shown by the fact that it oxidized to the colored compound when dissolved with dilute sodium hydroxide.

Although benzoic acid and acetamide both catalyzed the recombination of atomic hydrogen, we secured no evidence for any reaction between these two substances and the atomic hydrogen. The work on these solid compounds seems to indicate that the atomic hydrogen is only a comparatively mild reducing agent, and that it attacks the more easily reduced groups first.

---

[14] Copaux, Perepot and Hocart, *Bull. soc. chim.*, [4] **37**, 141 (1925).

[15] These were kindly furnished us by the E. I. du Pont de Nemours Co.

Reaction with Gaseous Organic Compounds.—In order to study gaseous organic compounds the apparatus was modified by placing a 750-cc. bulb between the discharge tube and the ground joint, the reactions being allowed to take place in this bulb. This bulb gave the gases a longer time in which to react and it may also prolong the life of the atomic hydrogen, since Kaplan[16] has shown that the life of atomic hydrogen is decidedly increased when the volume-to-surface ratio of the containing vessel is increased. To this bulb was sealed an inlet for the gases consisting of a capillary stopcock and small flask. The flask was attached to the stopcock by a ground-glass joint so that it could be removed in order to introduce volatile compounds. The rate at which vapors were introduced into the apparatus could be regulated by the size of the capillary and the temperature of the flask. Formic acid was found to catalyze the recombination of the hydrogen atoms. This was indicated by the increased temperature of the tube where the formic acid entered the apparatus. Color tests were secured for formaldehyde; the formic acid used did not give these tests. The amount of formic acid caught by the trap was determined by titrating with sodium hydroxide and it was found that very nearly all of the formic acid which entered the apparatus was recovered. It seems probable that the formic acid may have been decomposed by the hot glass walls to water and carbon monoxide and that the formaldehyde detected was the result of a reaction between carbon monoxide and atomic hydrogen. Bonhoeffer showed that in the case of oleic acid the COOH group is not attacked.

Freshly distilled acetaldehyde was polymerized to paraldehyde, but no further reaction could be detected except that the condensed material had a slightly yellow color, indicating that some decomposition or resinification had taken place. During these tests the bulb developed some active spots which became incandescent when the atomic hydrogen was led in. These glowing points were extinguished by the admission of acetaldehyde and they reappeared when the supply of acetaldehyde was cut off. The acetaldehyde seemed to "poison" these active spots.

It was noticed that when the acetaldehyde was first admitted to the bulb there was a flash of light, and if the supply was suddenly cut off, there was a similar flash. It was found that if just the correct amount of acetaldehyde was allowed to enter the bulb, a continuous glow could be maintained. The light was blue-green in color and when photographed with a small Hilger quartz spectrograph was found to consist of three bands in the region of 4000, 4250 and 4260 Å.; Bonhoeffer and Harteck[17] have found that saturated and unsaturated hydrocarbons react with atomic hydrogen with the emission of bands which lie in this region. Even with

---

[16] Kaplan, *Phys. Rev.*, **30**, 639 (1927).

[17] Bonhoeffer and Harteck, *Z. physik Chem.*, **139**, 64 (1928).

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.

BALTIMORE, MARYLAND

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

REACTIONS OF DISSOCIATED WATER VAPOR

BY H. C. UREY AND G. I. LAVIN

RECEIVED JUNE 22, 1929 PUBLISHED NOVEMBER 8, 1929

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

---

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