the chief means of activation at low pressure, and unless the mechanism of transfer of energy is very specific, we would expect the reaction rate to fall off during the course of a run as the products of reaction accumulate but practically this is not the case, though the run falls off in most cases to a very small extent. What the effects of simple local heating might be, and whether such an effect could be combined with our theory to give satisfactory results, we cannot at present decide.

Summary

Two theories based on collision hypotheses of quasi-unimolecular reactions, which we have previously developed, are applied to the decomposition of azomethane. It is possible to explain the falling off of the rate with pressure and to decide between the two theories. The efficiency of activation and deactivation at collision is considered, and the following are discussed: (1) the number of degrees of freedom involved in the various cases; (2) the effect of heat of reaction in the case of azomethane. The decomposition of diethyl ether is also considered briefly.

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

AN ATTEMPT TO PREPARE TRIATOMIC HYDROGEN[1]

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Introduction

The preparation and properties of an active modification of hydrogen, supposed to be triatomic, have been described by a number of investigators.[3] According to their papers, whenever hydrogen is ionized or dissociated a small amount of active product is formed. The activating agents that have been used with success include α-particles, the Siemens ozonizer, the vacuum discharge and the corona discharge. It has also been stated that if oxygen is burned in an atmosphere of hydrogen, or if hydrogen-oxygen mixtures containing deficiency of oxygen are detonated, part of the hydrogen remaining after the combustion is activated. It has furthermore been reported that hydrogen is activated by passage over

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[1] Extract from Dissertation submitted by Hugh M. Smallwood in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

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[3] (a) Duane and Wendt, *Phys. Rev.*, [2] **10,** 116 (1927); (b) Wendt and Landauer, THIS JOURNAL, **42,** 930 (1920); (c) **44,** 510 (1922); (d) Newman, *Phil. Mag.*, **43,** 455 (1922); (e) Venkataramaiah, *Nature*, **106,** 46 (1920); (f) **112,** 57 (1923); (g) *Chem. News*, **124,** 323 (1922); (h) THIS JOURNAL, **45,** 261 (1923); (i) Venkataramaiah and Swamy, *Proc. Sci. Ass. Mah. Coll. Viz.*, p. 23, Dec., 1922; (j) Grubb, *Nature*, 111, 600, 671 (1922); (k) Paneth, *Z. Elektrochem.*, **30,** 504 (1924); (l) Anderegg, THIS JOURNAL, **47,** 2429, (1925).

heated metals such as platinum and palladium. Of these various methods of preparation the passage of hydrogen over heated metals or through the ozonizer is said to be the most readily performed.

This modification of hydrogen has been reported to have the property of reducing sulfur, arsenic, phosphorus, nitrogen, etc., at room temperature to form the corresponding hydrides, and it is this characteristic that has been used to test for the material. It is not completely destroyed upon passage through glass wool, as is monatomic hydrogen, and it is described as having a period of half-life of the order of several minutes. It retains its activity upon condensation at liquid air temperatures and subsequent evaporation. Wendt and Landauer[3b,c] state that it is catalytically decomposed by platinum, nickel, copper, lead, antimony and cadmium, but that it is not affected by silver, molybdenum, mercury, tin, bismuth, zinc or aluminum. They further observed that its preparation in a closed system is accompanied by a decrease in pressure. It is this observation that has led to the assumption of a triatomic molecule.

Recent workers, however, have been unable to duplicate these results. Bach,[4] Scanavy-Grigoriewa[5] and Paneth, Klever and Peters[6] were unable to obtain evidence of activation upon passing hydrogen over heated metals. The latter authors also report unsuccessful attempts with the ozonizer, bombardment with α-particles and detonation of hydrogen-oxygen mixtures. Curtius,[7] moreover, was unable to obtain activation with the ozonizer. On the other hand Elliott,[8] working with a similar apparatus, reports a large number of positive results including quantitative studies of the effects of the conditions of the various experiments upon the extent of activation.

There are therefore many contradictions in the past work on active hydrogen. The present paper describes a series of experiments attempting the preparation of this active hydrogen. The methods of the former workers have been repeated and, in some cases, extended. Throughout the work the results have been negative.

Experimental

1. **Corona Discharge and Ozonizer.**—The apparatus used in these experiments and those to be described was built of Pyrex glass throughout. The corona tube was similar to that employed by Wendt and Landauer in the previous work on this method. It consisted of a Liebig condenser about 1 m. long. The high tension electrode was a bare aluminum wire, 0.6 mm. in diameter, strung along the axis of the central tube of the condenser by means of tungsten hooks, the latter being sealed through the glass at each end of the central tube. A salt solution circulated through the cooling jacket

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[4] Bach, *Ber.*, **58B**, 1388 (1925).

[5] Scanavy-Grigoriewa, *Z. anorg. allgem. Chem.*, **159**, 55 (1926).

[6] Paneth, Klever and Peters, *Z. Elektrochem.*, **33**, 102 (1927).

[7] Curtius, *Diss.*, Heidelberg, **1926**.

[8] Elliott, *Trans. Faraday Soc.*, **23**, 60 (1927).

served as the ground electrode. The central tube, through which the hydrogen passed, was 1.2 cm. in diameter. The tube was operated at a potential of 11–12 kv. with 60 cycle alternating current. This gave a fairly uniform discharge from the central wire.

The method used to determine the extent of activation was first developed by Wendt and Landauer.[3b,c] It is carried out as follows. After leaving the discharge the hydrogen is passed over glass wool (to remove atomic hydrogen) and is then mixed with nitrogen, the resulting mixture being scrubbed with 100 cc. of water. The presence of an active form of hydrogen results in the formation of ammonia, which is absorbed in the scrubbing water and determined by the usual Nessler test. The delicacy of this test was shown in the blank runs. These showed the absence of ammonia in the hydrogen and nitrogen used, but upon passing the hydrogen through the discharge without subsequent mixing with nitrogen, ammonia was found to be present to the extent of 0.0001% of the hydrogen passed. Presumably this was caused by the impurity of the original hydrogen. Both the hydrogen and the nitrogen were taken from cylinders, the nitrogen being bubbled through alkaline potassium pyrogallate and concentrated sulfuric acid.

Two thirty minute runs with this apparatus in which the pressure was maintained at one atmosphere and the temperature at room temperature, the rates of flow being 1400 and 180 cc. (0° and 760 mm.) of hydrogen per minute, respectively, failed to show an appreciable activation of the hydrogen in that the test for ammonia was no larger than that appearing in the blank run. The linear velocities of the gas flowing varied from 160 cm. to 1200 cm. per minute and the time spent in the ozonizer from 0.6 to 0.08 minute. This appears to be a sufficiently high velocity to insure removal from the activating zone and a sufficient time in the ozonizer to secure activation. Wendt and Landauer report only the volumes of hydrogen flowing per minute and not the dimensions of the apparatus, but from their description of their apparatus we believe that we have used both a wider range of linear velocities and times of activation than did these authors.

It was thought that this failure might be due to aluminum sputtered off the central electrode onto the glass walls. To remove this difficulty a Pyrex tube 4 mm. in diameter was inserted in place of the central electrode, being supported by a ring seal at each end. This tube was filled with salt solution and connected to the high tension terminal of a large spark coil. A uniform brush discharge throughout the tube was obtained with this set-up. Before commencing the actual runs the inside of the discharge tube was washed out with dilute hydrochloric acid and distilled water. Several half hour runs at atmospheric pressure and rates of flow of 400 to 800 cc. of hydrogen per minute gave no indication of the presence of an active form of hydrogen.

2. **Combustion of Oxygen in Hydrogen.**—The apparatus used was essentially the same as that employed by Venkataramaiah in the original work on this method. A large bulb was filled with hydrogen and the rate of flow of hydrogen through the bulb adjusted to a convenient value. Oxygen was then admitted through a platinum jet (8 mm. in diameter) and ignited by means of sparking points sealed through the wall of the bulb near the jet. The oxygen stream was regulated to give a flame about 3 cm. long. The products of combustion were passed through glass wool, over flowers of sulfur and finally directed against a piece of filter paper dipping into lead acetate solution. No formation of hydrogen sulfide could be detected with this apparatus.

3. **Passage of Hydrogen over Hot Wires.**—Hydrogen was passed over an electrically heated coil of nickel wire hung loosely from a horizontal porcelain tube. The temperature of the wire was varied from a dull red to the melting point of nickel. The rate of flow of hydrogen was varied through wide limits and in some experiments the gas was saturated with water by bubbling through water prior to entering the apparatus.

The hydrogen leaving the apparatus was led over flowers of sulfur and tested with lead acetate. No indications of the presence of an active modification of hydrogen were obtained although each new piece of nickel wire produced a very minute amount of hydrogen sulfide. In the light of the work of Bach and others (*loc. cit.*) these faint tests were interpreted as being due to some form of sulfur present in the original wire but which was soon exhausted.

Further experiments with platinum wires and the tungsten filament from a Mazda lamp gave no tests for hydrogen sulfide, although in some cases the wire was hot enough and the flow of hydrogen sufficiently great to melt the sulfur and even distil it into the lead acetate solution.

4. Vacuum Discharge.—The major part of the time spent on this research was devoted to an effort to determine whether or not an active modification of hydrogen capable of passing through a plug of glass wool is present in the gases drawn from a vacuum discharge.

Throughout this part of the work electrolytic hydrogen was used, the electrolyte being a 30% solution of potassium hydroxide. The hydrogen was passed through asbestos to remove as much as possible of the alkaline spray, and then passed over heated platinized asbestos to remove any trace of oxygen. In some experiments the hydrogen was dried with liquid air.

The first apparatus set up was, as nearly as possible, an exact replica of that used by Wendt and Landauer. This consisted of a discharge tube 10 cm. long from which the hydrogen was led over glass wool, then over flowers of sulfur and finally over a strip of filter paper dipping in lead acetate solution. No hydrogen sulfide was formed in this apparatus upon running it for as long as half an hour, although Wendt and Landauer report large tests at the end of three minutes. The pressure in the discharge was varied from 2 to 7 cm. of mercury and the rate of flow of hydrogen was varied through a wide range.

This method of detecting a small amount of hydrogen sulfide does not seem particularly delicate. To remedy this defect and to permit working at lower pressures another procedure was developed. The lead acetate bubbler was replaced with a trap filled with silica gel, which was activated by heating at 300–350° for one hour in a current of hydrogen at a pressure of 1–2 mm. The apparatus was then filled with hydrogen at atmospheric pressure and the gel heated for another fifteen minutes in a slow current of hydrogen which was led out of the apparatus and bubbled through a solution of lead acetate acidified with acetic acid. This was done to show that all of the sulfur had been removed from the gel. If this blank was satisfactory a run was made during which the gel was cooled with liquid air. At the conclusion of the run the apparatus was again filled with hydrogen and the heated gel swept out into the lead acetate solution as before. Although much more laborious than the methods used by previous workers, this procedure enabled the detection of exceedingly minute amounts of hydrogen sulfide.

On using this more delicate test it was found to be extremely difficult to obtain good blank tests. Commercial flowers of sulfur were found to contain fairly large amounts of volatile sulfides. To remedy this a very pure form of sulfur was prepared by acidifying a solution of sodium thiosulfate with hydrochloric acid and filtering off and distilling the precipitated sulfur. It was next found that in the course of a thirty-minute run enough sulfur could distil over into the gel to give fairly large amounts of lead sulfide, the elementary sulfur, of course, being reduced upon passing through the heated gel in the presence of hydrogen. This effect was eliminated by adjusting the Dewar flask holding the liquid air, in which the gel was immersed, in such a manner that the liquid air level stood 5–10 cm. above the top of the gel. The sulfur condensed to an opalescent film immediately upon reaching the cold tube. Upon removing the liquid air the hydrogen sulfide evaporated and could be swept out of the gel by heating without disturbing the sulfur condensed some distance away. Employing these precautions it was found possible to obtain perfect blank tests both upon running the discharge with no sulfur in the apparatus and upon passing the hydrogen over the sulfur in the absence of the discharge.

In the course of an actual experiment the hydrogen passed out of the discharge, through a plug of glass wool 10 cm. long and finally over the sulfur. At this point any of the active form present would react to form hydrogen sulfide, which would be adsorbed on the gel and would, at the end of the experiment, be made evident by the precipitation of lead sulfide. Such experiments frequently resulted in the formation of a small amount of precipitate but the tests so obtained were so minute and erratic that they could not be definitely ascribed to the presence of an active modification of hydrogen.

The conditions under which the various experiments were carried out were as follows. The pressure was varied in different runs from 1 to 80 mm. At the lower pressures rates of flow of 20–30 cc. per minute were used and at the higher pressures the rate was maintained at 200 cc. per minute, both volumes being measured under standard conditions. Throughout the low pressure work Wood[9] discharge tubes about 1 m. long were used. These were run with wet hydrogen, giving the red discharge due to atomic hydrogen, and with dry hydrogen, in which case the secondary spectrum was most prominent. The hydrogen to be tested was tapped off either in the middle of the tube or near one of the electrodes, since Smyth and Brasefield[10] have found that at that point in the discharge there are large amounts of H_3^+. The sulfur was inserted 15–30 cm. away from the discharge, connection being made with 7mm. glass tubing. In some of the experiments the discharge tube was cooled with tap water, with salt-ice mixture or with carbon dioxide snow and ether.

The experiments at higher pressures were carried out in smaller discharge tubes of the general type used by Wendt and Landauer. These were water cooled throughout. In some cases a condensed discharge was used, producing the atomic spectrum at a pressure of several centimeters.

During the whole series of experiments sporadic tests were obtained but these were so small that it was necessary to run for thirty minutes or more in order to produce a visible amount of lead sulfide. The size of the tests seemed to have no connection at all with the experimental conditions under which they were obtained. Efforts to show that the substance producing them was unstable enough to decay when led through a by-pass 4 m. long and 2 cm. in diameter before reaching the sulfur were not conclusive because of the strong fatigue effect observed in all the tubes. Attempts to rejuvenate a spent tube by washing with dilute hydrochloric acid, sodium hydroxide and distilled water were only partially successful. The great difficulty encountered in the whole work was that it was not possible to make a series of consistent runs in order to determine, for example, whether or not cooling the discharge had any effect on the size of the precipitate. No tube could be found that, when operated under identical experimental conditions, would give the same amount of lead sulfide three times in succession.

Wendt and Landauer have sought to obtain evidence for their assumption of a triatomic molecule by showing that the activation of hydrogen in a closed system is attended with a decrease in pressure. This experiment has been repeated and part of the original results confirmed. The apparatus used consists of a U-shaped discharge tube equipped with platinum electrodes and attached to a small closed arm manometer. If a discharge is passed at a hydrogen pressure of 9 cm. of mercury and at liquid air temperatures, there is a considerable pressure drop provided the electrodes are immersed

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[9] Wood, *Proc. Roy. Soc.* (*London*), **97**, 455 (1920).

[10] Smyth and Brasefield, *Proc. Nat. Acad. Sci.*, **12**, 443 (1926).

in the liquid air. If, however, the electrodes are not immersed in liquid air there is no effect. Wendt and Landauer report that the discharge has a yellow or greenish yellow color. In the repetition the discharge was the usual pale blue color throughout.

Discussion

The experiments just described indicate that, under the experimental conditions detailed, there is no appreciable activation of hydrogen. The failure of duplication of the results of the original workers may be accounted for in a number of ways. In the first place none of the papers announcing positive results report adequate blank experiments. All of the investigators were careful to ensure the absence of the particular hydride which was later to form the test from the hydrogen used in the work, but none report experiments designed to show that there was no source of sulfur or nitrogen, as the case might be, sufficiently near to the activating agent to cause the tests. Thus a little elementary sulfur blown back into a discharge can account for many of the results ascribed to H_3. On the other hand, the experiments described by Duane and Wendt and by Wendt and Landauer were so numerous and of such varied nature that it is difficult to account for them by assuming contamination of the apparatus. Although Elliott's results are detailed and self-consistent they are open to criticism on the ground that he did not sufficiently guard against the possibility of sulfur dust being blown back into the discharge. If his results were due to an active hydrogen, they fail to check those of previous workers in a number of instances. Thus he finds a much shorter period of half life than that reported by Duane and Wendt. This fact suggests a correlation between his work and that of Anderson[11] and of Mitchell and Marshall,[12] who found that the temperature at which copper oxide begins to react with hydrogen is decreased if platinum is placed in the hydrogen stream a short distance in front of the copper oxide. They showed that the effect was due to an unstable modification of hydrogen with an extremely short life. It is possible that some of these positive results may have been due to hydrogen molecules in metastable vibrational and rotational state. The question of blank tests, however, certainly deserves more attention than it has received. All of the papers, excepting the two last cited, in which the necessary controls are reported, record uniformly negative results.

An unknown catalytic effect might account for the uncertainty of the results. This could hardly be an anticatalytic effect since cylinder hydrogen has been used successfully. On the other hand, the hydrogen used in the greater part of the previous work could only have contained minute traces of water vapor, nitrogen or argon. The hydrogen used in the present work must have contained all of these gases as impurities

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[11] Anderson, *J. Chem. Soc.*, **121**, 1153 (1922).

[12] Mitchell and Marshall, *ibid.*, **123**, 2448 (1923).

at one time or another. It seems unlikely that it is a question of the catalytic effect of the walls of the apparatus since, if this were the case, it should have been observed by the first workers in the field.

The pressure drop experiments fail to add any evidence since hydrogen is readily taken up by metallic electrodes and may be driven into the glass walls to an appreciable extent. In this connection it is interesting to note that in 1908 Fischer and Iliovici[13] subjected hydrogen at atmospheric pressure and liquid air temperatures to the silent discharge in a tube with *external* electrodes. They found a decrease in pressure of 0.5 mm. but, since this was less than their experimental error, they concluded that there is no new molecular species formed under these conditions. Wendt and Landauer's work would lead one to expect a large pressure drop in such an experiment. Furthermore, the pressure drop observed by them and duplicated by us was so large that, had it been due to the formation of H_3, it is extremely unlikely that the other experiments with the vacuum discharge would have been negative.

The only conclusion that can be drawn, therefore, is that the existence of triatomic hydrogen has not yet been established. Assuming that there is such a substance, however, it is more difficult to prepare than has been formerly supposed.

Summary

1. Unsuccessful attempts to prepare H_3 by means of the corona discharge, ozonizer, combustion of oxygen in hydrogen, passage of hydrogen over hot metals and the vacuum discharge are described.

2. The previous work on this subject is discussed with the conclusion that the existence of H_3 is not as certain as has been supposed.

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[13] Fischer and Iliovici, *Ber.*, **41**, 4452 (1908).