THE CHEMICAL REACTIONS OF HYDROGEN ATOMS[1]

BY HUGH S. TAYLOR

During the last two decades a revolution has occurred in the chemistry of hydrogen, largely through the initial efforts of the physicist. With the method of positive-ray analysis, the existence of H_3 was demonstrated by Sir J. J. Thomson.[2] With the high-tension discharge and spectroscopic evidence as auxiliary, Wood[3] succeeded in producing hydrogen atoms. With excited mercury atoms suffering inelastic collisions with hydrogen molecules, hydrogen atoms also result, as was shown by Cario and Franck.[4] The chemical properties of H_3 are still very obscure but those of the atomic species are relatively clear and readily understood, probably by reason of the pioneering work of Langmuir[5] in the investigation of the "clean-up" of hydrogen in tungsten filament lamps. Langmuir showed that, at the temperature of incandescent tungsten filaments, hydrogen at low pressures was appreciably dissociated into atoms and that the atomic species had remarkable and characteristic properties. Hydrogen atoms were adsorbed tenaciously by glass surfaces causing the "clean-up" effect, the diminution of pressure within the system. Furthermore, they could reduce metallic oxides, such as copper oxide and tungstic oxide, at room temperatures to the metallic state. Finally, the quantitative data showed that the atoms recombined with the liberation of some 97.5 kg. cals. of energy. The importance of this original work is manifest in the sequel, since it is by reason of these several properties, found by Langmuir, that the presence of hydrogen atoms was distinguished by Wood and by Cario and Franck. The latter used the "clean-up" and the reducibility of metallic oxides to identify the hydrogen atoms resulting from collision with excited mercury. Wood identified the atomic species by the energy liberated in its catalytic recombination, the striking application of which in hydrogen flames has already been demonstrated by Langmuir.[6]

The Reaction of Hydrogen Atoms Produced by Wood's Method.— That Wood's method, the high-tension discharge through moist hydrogen, was capable of giving sufficient hydrogen for an examination of the chemical

[1] Presented at the General Session of the Sesqui-Centennial Meeting of the American Chemical Society, Philadelphia, September, 1926.

[2] Thomson, "Rays of Positive Electricity," Longmans, Green and Co., 1913, p. 116.

[3] Wood, Proc. Roy. Soc., 102A, 1 (1923).

[4] Cario and Franck, Z. Physik, 11, 162 (1922).

[5] Langmuir, Trans. Am. Electrochem. Soc., 20, 225 (1911); THIS JOURNAL, 34, 860 (1912); 36, 1708 (1914); 37, 417 (1915).

[6] Langmuir, Gen. Elec. Rev., 29, 153 (1926).

properties of the atoms in detail, was indicated by Wood himself; he pointed out that the atoms were capable of converting an unsaturated oil into a solid saturated fat, a process paralleling the industrial catalytic process of fat-hardening. Taylor and Marshall[7] saw in Wood's method a means of investigating the mechanism of the hydrogen-chlorine combination suggested by Nernst. According to Nernst, the photochemical combination of these two gases possibly occurred by a succession of reactions, thus: $Cl_2 + light = 2Cl$; $Cl + H_2 = HCl + H$; $H + Cl_2 = HCl + Cl$, the last two reactions forming a so-called chain of reactions which could continue over a long succession of impacts since, in each, an active atom is produced. To test this hypothesis, Taylor and Marshall introduced hydrogen atoms prepared by Wood's method, into unilluminated chlorine and showed that hydrogen chloride was formed. Marshall[8] subsequently showed that more hydrogen chloride was produced than would correspond to the hydrogen atoms introduced into a hydrogen-chlorine mixture, thus establishing experimentally the possibility of the Nernst mechanism of reaction chains.

Bonhoeffer's Researches.—A comprehensive examination of the chemical properties of hydrogen atoms produced by Wood's method has been conducted by Bonhoeffer.[9] He first examined the reactivity of hydrogen atoms with solid bodies. He showed that a wide variety of metallic oxides and salts were rapidly and completely reduced to the metallic state and that the metals so produced acted as catalysts for the recombination of hydrogen atoms. In this manner he was able to compare the catalytic activity of a large number of metals and established that the order of activity was practically that of the hydrogen overvoltage series, confirming a prediction of Bancroft. Thus, metals showing low overvoltage for hydrogen, such as platinum, palladium and nickel, were among the best catalysts, while metals with too high overvoltage, such as gold, mercury and lead, showed the least catalytic activity for recombination of hydrogen atoms. We shall return to this point subsequently.

Bonhoeffer showed that hydrogen atoms react readily with the metalloids such as sulfur, arsenic, phosphorus, giving the corresponding hydrides. By determining the amount of reaction with these bodies at various distances from the generating source, and from the velocity of gas flow, Bonhoeffer calculated a half life period of about 1/3 sec. at about 0.5 mm. pressure. While the exact value has not been thus ascertained it is certainly true that hydrogen atoms in the gas phase suffer a large number of collisions (probably more than 10^4) before union to molecules occurs. The reason for the relatively great stability of hydrogen atoms, away from

[7] Taylor and Marshall, *Nature*, **112**, 937 (1923).

[8] Marshall, *J. Phys. Chem.*, **29**, 842 (1925).

[9] Bonhoeffer, *Z. physik. Chem.*, **113**, 199, 492 (1924).

a surface, has aroused a considerable theoretical discussion,[10] involving the problem of three body collisions and also the application of the quantum theory.

More recently, Bonhoeffer[11] has studied the reaction of hydrogen atoms with gases and has confirmed, with the product of Wood's method, the results obtained somewhat earlier by a number of workers using the method of Cario and Franck. Several of these will be discussed in detail in subsequent pargraphs. Bonhoeffer's results may be summarized. He confirmed the results of Taylor and Marshall with chlorine and bromine. He showed that an energetic heat effect was produced on admixing hydrogen atoms with a hydrogen halide probably by reason of a sequence of reactions involving several stages but ultimately yielding, in the case of hydrogen chloride, only hydrogen molecules and the halide. With hydrogen bromide some bromine was formed. It is evident, therefore, that with a hydrogen halide, the first reaction stage is $H + HX = H_2 + X$. He also confirmed the observation of Taylor and Marshall that, with carbon monoxide, hydrogen atoms yield formaldehyde. His yields were puzzlingly low for reasons subsequently elucidated by Marshall and to be set forth later. Hydrogen atoms reduced carbon dioxide, yielding also some formaldehyde. With oxygen Bonhoeffer found hydrogen peroxide as a primary product as reported somewhat earlier by Taylor, Marshall and Bates using the Cario-Franck method. The important observation was also made that hydrogen atoms do not react with nitrogen to form ammonia. This observation checks that of Taylor and Marshall with the Cario-Franck method at room temperature but it is not in agreement with the results of Noyes[12] at the boiling point of mercury. It suggests that, in catalytic ammonia synthesis, nitrogen must also be activated. It was further shown that hydrogen atoms show no heat effect when brought into contact with ammonia molecules. The correlation of this with the behavior of hydrogen atoms towards hydrogen halides suggests to the writer a reason for the observations of Hinshelwood and Burk that hydrogen retards the decomposition of ammonia at platinum surfaces while it does not retard the decomposition of hydrogen iodide. Evidently, platinum-hydrogen complexes are even less readily decomposed by ammonia than hydrogen atoms whereas, apparently the reaction, $Pt - H + HI = Pt + H_2 + I$, can occur.[13]

Two other gases, in addition to ammonia, are indifferent to hydrogen atoms; these are methane and water vapor. In neither case is there any thermal evidence of reaction. This is in agreement with what we know

[10] See, for example, Franck, Z. Elektrochem., **31**, 350 (1925); Bodenstein, ibid., **31**, 343 (1925).

[11] Bonhoeffer, Z. physik. Chem., **119**, 385, 474 (1926).

[12] Noyes, THIS JOURNAL, **47**, 1003 (1925).

[13] See H. S. Taylor, Proc. Roy. Soc., forthcoming publication.

concerning the stability of the several linkages, N—H in ammonia, C—H in saturated hydrocarbons and H—OH in water.[14]   Each of these linkages is of the same order of thermal magnitude as the H—H linkage in molecular hydrogen.   This does not extend to hydrogen sulfide, since Bonhoeffer showed that there was an energetic thermal effect when hydrogen atoms were admixed with this gas; probably the initial action is H + H_2S = H_2 + SH.

The Chemical Reactions of Hydrogen Atoms Produced by the Cario-Franck Method

The Cario-Franck method of producing hydrogen atoms was employed by Dickinson[15] to show that, at room temperature and 45°, hydrogen and oxygen combine to form water.   Taylor and Marshall[16] very considerably simplified the technique of the Cario-Franck method by conducting experiments at normal pressures instead of at the low pressures (0–20 mm.) employed by Cario and Franck and by Dickinson.   The reactions can be induced very simply by allowing a mixture of the reacting gas with hydrogen, in contact with liquid mercury, or saturated with mercury vapor at the reacting temperature, to be illuminated directly with the light of a mercury arc, the mercury electrodes of the arc being cooled by immersion in cold water or by other suitable means.   Reaction is sufficiently rapid so that progress of the reaction can be followed with an ordinary manometer or by analysis of the products.   Both static and dynamic methods of study may be employed.

Arc Systems.—Marshall[17] has described a quartz system suitable for both static and dynamic methods.   Mr. Bates, in the writer's Laboratory has developed a reaction system very suitable for flow methods of investigation.   It has the advantage that it dispenses with expensive quartz arcs and utilizes one which can readily be made in the laboratory out of glass. The arc system is adapted from a design of Langmuir,[18] used in his studies of the characteristics of electrical discharges through mercury vapor. The arc is built around a quartz tube X which forms either the reaction system or, preferably, the outer jacket of a water cooling system for Y, the quartz reaction vessel proper.   This is evident from Fig. 1.

The arc system surrounding the quartz consists of a source of mercury vapor caused by arcing across the two mercury pools A and B.   The anode C is cone shaped and serves to deflect any mercury atoms shot from the pools of mercury.   If the bulb containing this cone be kept in water at a controlled temperature, the vapor pressure of mercury in the arc system is thereby kept at the saturation concentration at that temperature.

[14] See Senftleben, *Z. Physik*, **37**, 529, 539 (1926).

[15] Dickinson, *Proc. Nat. Acad. Sci.*, **10**, 429 (1924).

[16] Taylor and Marshall, *J. Phys. Chem.*, **29**, 842 (1925).

[17] Marshall, *J. Phys. Chem.*, **30**, 26 (1926).

[18] Langmuir, *Gen. Elec. Rev.*, **27**, 538 (1924); *C. A.*, **19**, 1531 (1925).

The arc may readily be extended from C to D and D_2 two nickel cup-shaped electrodes, welded to tungsten leads, by breaking down the space charge with an ordinary spark coil, adjusting the applied potential between A and D_1 and D_2, to obtain the desired lamp characteristics. We have operated such lamps with a voltage drop of 35 volts along an arc path 50 cm. long with currents as high as 20 amperes divided equally between D_1 and D_2. The mercury boiler is best maintained at a temperature of 50-70°.
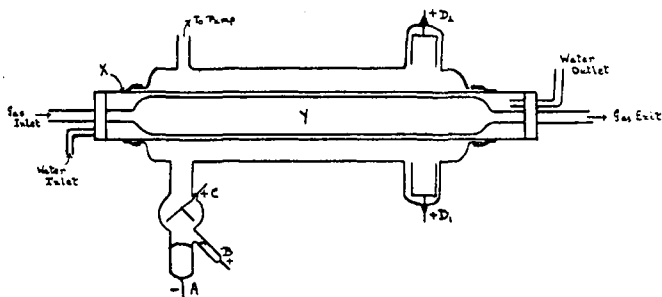

Fig. 1.

Under such circumstances abundant resonance radiation is received in the reaction system.

Simple quartz mercury arcs, modeled upon the same pattern, have been employed by the writer in conjunction with Mr. J. L. Whitten in these studies.

The make-up of the lamp is readily seen from Fig. 2, the quartz portion in the center being readily constructed with the aid of two quartz-Pyrex seals. The anode and cathode compartments are made of G-702 P glass. Such an arc 40 cm. long and 12 mm. in diameter operates at 50 volts and 8 amperes with the mercury vapor saturated at 30°.
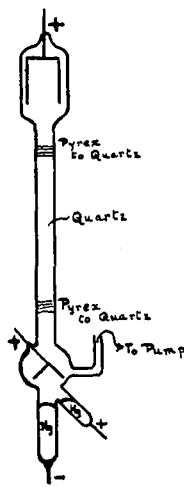

Fig. 2.

Hydrogen Peroxide and Formaldehyde.—In such systems, the Princeton investigations have shown that hydrogen atoms react with oxygen to form hydrogen peroxide as an initial isolable product which, upon further exposure to the ultraviolet light, decomposes to yield water. With carbon monoxide, formaldehyde is formed, more than 75% of the hydrogen disappearing being recoverable as formaldehyde vapor. With ethylene, quantitative hydrogenation occurs with formation of ethane. Nitrous oxide is reduced, but the reduction products are complex. With nitrogen, even with intense sources of resonance radiation, we have never been able to detect ammonia and are completely at a loss to account for the origin of Hirst's[19] ammonia, since our observations accord with those of Bonhoeffer. We believe that Hirst's positive test for hydrazine may possibly be due to formaldehyde from a trace of carbon monoxide in the hydrogen. Carbon

[19] Hirst, *Proc. Cambridge Phil. Soc.*, **23**, 162 (1926).

dioxide which we earlier reported to be unacted upon by hydrogen atoms has now been shown by Marshall to react slowly, at a rate approximately 2% of that found with carbon monoxide. Carbon monoxide and oxygenated organic compounds are present in the product.

Marshall[20] has subjected the reactions with oxygen and with carbon monoxide to an intensive study. He has shown that in the reaction with oxygen the rate is approximately proportional to the molecular fraction of hydrogen. Hydrogen peroxide is the first isolable product and measurements of the light absorption of reacting systems lead to the conclusion that at least 6.6 molecules of hydrogen peroxide are produced per quantum of light energy of wave length 2536.7 Å. absorbed. With carbon monoxide, 6 molecules of formaldehyde per quantum are absorbed, these several values representing minimal values, any further corrections serving to increase this ratio. The kinetics of the latter reaction differs from that producing hydrogen peroxide. The results obtained indicate that the velocity is determined by the equation, $+d(HCHO)/dt = k(P_{H_2})^{1/2}(P_{CO})$. Such an equation points clearly to the fact that atomic hydrogen is one of the constituents taking part in the reaction. If this is the correct equation for the reaction, the velocity with a given gas mixture should be proportional to the three-halves power of the total pressure. The writer is conducting such investigations at the present time in the pressure range, 0–100 atmospheres.

Evidence in Favor of Atoms.—Olson and Meyers[21] in a kinetic study of the hydrogenation of ethylene also conclude that the rate of reaction, over a pressure range from 1.5 to 11 mm. of hydrogen, is proportional to the square root of the hydrogen pressure, additional evidence that the atomic species is an important constituent of the reaction system. This point has acquired some importance by reason of the suggestion of Rideal and Hirst[22] that the mercury simply produces excited molecules of hydrogen by the collision process and that it is these excited hydrogen molecules which undergo reaction with the various species. It does not, however, seem to be possible to maintain this position in view of the parallel results of Bonhoeffer with atoms produced by Wood's method. Furthermore, as Senftleben[23] has shown, a system containing hydrogen and mercury, illuminated with the resonance radiation, gives an increased thermal conductivity, explainable by the presence of hydrogen atoms.

Hydrogen Atoms by Electrolysis.—That these reactions involve hydrogen atoms can be concluded from one other line of evidence. In an earlier paragraph it was pointed out that the order of catalytic activity of the metals for the recombination of hydrogen atoms was the order of the

[20] Ref. 17, pp. 34, 1078 and forthcoming paper.
[21] Olson and Meyers, THIS JOURNAL, **48**, 389 (1926).
[22] Rideal and Hirst, *Nature*, **117**, 444 (1926).
[23] Senftleben, *Z. Physik*, **32**, 922 (1925).

hydrogen overvoltage series. Now, Bancroft and others have related overvoltage to the speed at which atomic hydrogen, produced by the discharge of hydrogen ions, is catalytically converted to the molecular state. The correlation actually found between measurements of catalytic action and overvoltage suggests, therefore, that one might obtain the reactions of hydrogen atoms under suitable circumstances at the discharge of hydrogen ions at electrodes. If the discharge process is $H^+ + \ominus = H$, followed by $2H = H_2$, it should be possible, especially at electrodes showing high overvoltage or feeble catalytic activity for the molecule-producing process, to demonstrate there the existence of hydrogen atoms. A glance at the literature dealing with "nascent" hydrogen shows this to be correct. One of the most striking cases only will be cited—the production of hydrogen peroxide.

We have shown that hydrogen produced by Wood's method or by that of Cario and Franck reacts readily at room temperatures with oxygen molecules to yield hydrogen peroxide. Now, if the active hydrogen be atomic, it ought to be possible to produce hydrogen peroxide by bubbling oxygen over a cathode at which hydrogen is being liberated. This method of producing hydrogen peroxide has been known since 1882, when M. Traube[24] showed that hydrogen peroxide is formed in small quantities at the cathode, not the anode, during the electrolysis of aqueous solutions, provided oxygen is bubbled about the cathode. If air or oxygen be carefully excluded from the cathode, no hydrogen peroxide is formed. Still more convincing are the observations of Fischer and Priess,[25] who studied this reaction with oxygen at 100-atm. pressure bubbling past the electrode. They found that over 90% of the hydrogen theoretically produced by electrolysis in the early stages of the process could be recovered as peroxide. Furthermore, as most suitable cathode material, they found amalgamated gold electrodes, two elements obviously well suited to delaying the catalytic recombination of hydrogen atoms and thus facilitating reaction with oxygen. There seems little doubt, therefore, that in all these cases, we are dealing with the reactivity of the atomic species. The well-known experiment of Traube, who allowed a jet of burning hydrogen to impinge on the surface of ice and showed the presence of hydrogen peroxide, would, accordingly be interpreted as the reaction between hydrogen atoms, produced in the flame by thermal dissociation, and oxygen molecules present in the flame. This mechanism differs somewhat from that suggested by Lewis and Randall[26] on the basis of their free-energy calculations.

The parallelism between cathodic reductions and catalytic hydrogena-

[24] Traube, *Ber.*, **15**, 2434 (1882); *Sitzb. Akad. Berlin*, **1887**, p. 1041.

[25] Fischer and Priess, *Ber.*, **46**, 698 (1913).

[26] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, **1923**, p. 496.

tions and reductions is too exhaustive a theme to enlarge upon here; but there is an increasing body of evidence that, in many reactions, in both cases, atomic hydrogen is involved.

The Mechanism of the Cario-Franck Method of Producing Atoms.— Two possibilities are evident in the production of hydrogen atoms by collision with an excited mercury atom. The energy of such an atom, having a quantum of energy corresponding to $\lambda = 2536.7$ Å., is 112 kg. cals. and is, therefore, sufficient to cause the disruption of the molecule into two atoms a process which requires an energy between 96.5 kg. cals.[6] and 107 kg. cals.[27] according to two recent estimates. In such a case we might write the process thus: $H_2 + Hg' = Hg + 2H$. An alternative mechanism is possible whereby the primary products would be mercury hydride and one hydrogen atom, $H_2 + Hg' = HgH + H$. The former mechanism might involve the Rideal-Hirst assumption of an excited hydrogen molecule as an intermediate stage: $Hg' + H_2 = Hg + H_2'$ $= Hg + 2H$. It is difficult to see how the second postulated mechanism could ever yield an excited hydrogen molecule.

Some experiments by Compton and Turner[28] on the band spectra in mercury discharge tubes point to the presence of mercury hydride and to the second mechanism postulated. This evidence is now being supplemented by an examination of the behavior of excited mercury in the presence of other gases than hydrogen. The evidence points to the conclusion that excited mercury actually functions as a dehydrogenation agent and enters into combination with the fragments of the disruption process. The most convincing of this evidence is in a recent paper by Senftleben,[14] who shows that excited mercury brings about the dissociation of water vapor, the product identified being hydrogen. Senftleben assumes the process to be $Hg' + HOH \longrightarrow Hg + H + OH$, but is unable to trace the subsequent history of the hydroxyl group. Olson and Meyers[21] in their study of the polymerization of ethylene by excited mercury atoms drew attention to an initial increase in pressure. Mr. J. R. Bates has investigated this at atmospheric pressure and has shown that volatile mercury organic compounds, acetylene and hydrogen can result from this reaction, the excited mercury reacting, therefore, as a dehydrogenation agent. Other examples, such as the saturated hydrocarbons, ammonia and hydrogen sulfide are under study, from the results of which more definite information as to the role of excited mercury and as to the mechanism of collisions of the second kind may be gained.

Summary

1. The chemical properties of hydrogen atoms prepared by Wood's method and that of Cario and Franck have been detailed.

[27] Bodenstein and Jung, Z. physik. Chem., **121**, 127 (1926).

[28] Compton and Turner, Phil. Mag., **48**, 360 (1924).

2. Two mercury-arc systems suitable for the preparation of hydrogen atoms have been described.

3. The presence of hydrogen atoms at cathodes during electrolysis as well as in oxyhydrogen flames has been indicated.

4. The mechanism of the Cario-Franck method has been discussed and further lines of study have been outlined.

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DISPLACEMENT OF METALS FROM SOLUTIONS OF THEIR SALTS BY LESS ELECTROPOSITIVE ELEMENTS. III. THE ACTION OF LIQUID AMMONIA SOLUTIONS OF SALTS OF THE ALKALI AND ALKALINE EARTH METALS ON MAGNESIUM AND OTHER ELEMENTS[1]

BY F. W. BERGSTROM[2]

Introduction

A metal in general precipitates a less electropositive metal from solutions of its salts. Thus, as copper reacts with mercuric nitrate in water solution to form metallic mercury and cupric nitrate, so we should expect sodium or potassium to displace the less electropositive elements calcium, barium, magnesium and aluminum from water solutions of their salts were it not for the vigorous action of the alkali and alkaline earth metals with water. Indirect evidence that such replacements take place has been obtained by G. McPhail Smith and his pupils[4] who have shown that aqueous solutions of salts of sodium and barium, for example, react with potassium amalgam in the manner represented by the equations, $K + NaI \rightleftharpoons KI + Na$ and $2Na + BaCl_2 \rightleftharpoons Ba + 2NaCl$. Jellinek, with Czerwinski and others, has shown that similar reactions take place in fused salt media.[5] Thus, barium reacts with fused sodium chloride in accordance with the equation, $Ba + 2NaCl \rightleftharpoons 2Na + BaCl_2$, while, inversely, sodium reacts with barium chloride in accordance with the above equation read from right to left.

A direct study of reactions of this type at ordinary temperatures may be carried out in liquid ammonia, in which the alkali and alkaline earth metals dissolve as such with the formation of relatively stable blue solu-

[1] Papers of this series previously published are (a) THIS JOURNAL, 45, 2788 (1923); (b) 47, 1836 (1925).

[2] National Research Fellow.

[3] A preliminary version of this paper was received on September 2, 1925. (Editor.)

[4] (a) Smith, Am. Chem. J., 37, 506 (1907). (b) Smith and Rees, THIS JOURNAL, 40, 1802 (1918). (c) Smith, ibid., 37, 76 (1915). (d) Smith and Ball, ibid., 39, 179 (1917); and other articles.

[5] Jellinek and Czerwinski, Z. physik. Chem., 110, 192 (1924).