HYDROGEN ATOMS, OXYGEN ATOMS 134

HYDROGEN ATOMS, OXYGEN ATOMS,* AND THE HYDROXYL RADICAL.

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Hydrogen Atoms.

Molecular hydrogen is easily dissociated into atoms under suitable conditions, and by means of a gas discharge tube it is possible to produce a high percentage of atomic hydrogen and conveniently study its pro-That hydrogen atoms are present in a discharge through perties. hydrogen at about I mm. pressure is clear from the emission under these conditions of the Balmer spectrum, of which atomic hydrogen is the source, and it is also clear from the work of Wood¹ that under such appropriate experimental conditions the percentage of atomic hydrogen is considerable. This procedure was obviously very convenient for producing hydrogen atoms for chemical purposes, and has been utilised by Bonhoeffer and his co-workers² to such good effect that our knowledge of the physical and chemical properties of hydrogen atoms is now more complete than that of any other free atom or radical.

Before discussing the chemical reaction of the atoms it is worth noticing that at a pressure of I/10 mm. they have a life of about I sec. and therefore do not re-unite at once to form normal molecular hydrogen. From this lifetime one can conclude that under these conditions not more than one collision in a million between two atoms leads to the formation of a molecule. It is also easy to show that under these conditions about every millionth is a three-body collision. It is therefore reasonable to assume that this reformation of molecular hydrogen is indeed a three-body process. It is always important to remember that

* This paper is taken in part from Grundlagen der Photochemie, Bonhoeffer

¹ R. W. Wood, *Phil. Mag.*, **42**, 729, 1921; **44**, 538, 1922.
² K. F. Bonhoeffer, *Z. Phys. Chem.*, **113**, 199, 1924; Boehm and Bonhoeffer, *Z. Phys. Chem.*, **119**, 385, 1926. *Cf. K. F. Bonhoeffer, Zusammenfassende Darstellung, Erg. exakt. Naturw.*, **204**, 1927.

P. HARTECK

hydrogen atoms readily reunite on the walls of the reaction vessels and in particular on any catalytic metal surface. In the experiments to be described a stream of hydrogen, rich in atoms, was produced at a pressure of from 1/10 to 1 mm., mixed with the gas with which it was to react, and the products studied.

With hydrogen, the interaction between atomic and molecular hydrogen itself can actually be studied, since the reaction $H+H_2 \rightarrow H_2+H$ can be followed by using para-hydrogen in place of ordinary hydrogen.³ From the measured rate of transformation of para-hydrogen into orthohydrogen, the rate of interaction of atomic and molecular hydrogen can be found. About I in 500,000 collisions are effective at ordinary temperatures, more as the temperature increases, and the activation energy is about 7 Cals. By assuming these numbers, this reaction may be used as a method of finding the number of H atoms present as intermediate products in a photochemical, or other, reaction.

By mixing small amounts of oxygen with H-atoms it can be shown that there is no rapid reaction and that indeed at pressures of I mm H-atoms are stable in the presence of oxygen for at least I/IO sec. In other words, in these experimental conditions at the most I in 10⁵ collisions between an atom of hydrogen and a molecule of oxygen leads to any reaction. A high yield of hydrogen peroxide is, however, obtained when a vessel cooled with liquid air is attached.⁴

Water vapour does not interact with H-atoms. This is to be expected, since the two conceivable reactions

 $\begin{array}{l} H_2O \,+\, H \,\rightarrow H_2 \,+\, OH \\ H_2O \,+\, 2H \,\rightarrow \, 2H_2 \,+\, O \end{array} \right\} \text{ are both too endothermic.}$

Nitrogen and H-atoms give no ammonia, since the reaction, $N_2 + H \rightarrow NH + N$, is strongly endothermic, and the three-body collisions, $N_2 + 2H \rightarrow 2NH$, is still endothermic, while the presence of NH as an intermediated product in any formulation for the production ammonia in the gas phase seems unavoidable. Similarly, $N\dot{H}_3$ and H-atoms do not react at room temperature. The heat of the reaction $NH_3 + H \rightarrow NH_2 + H_2$ is uncertain, but can be roughly estimated to be about - 15 Cals. Nor will hydrogen atoms react with carbon monoxide or dioxide at pressures of about $\frac{1}{2}$ mm. to any appreciable extent, though it is possible to collect small amounts of formaldehyde during a long experiment. The mechanism of the reaction must as yet remain uncertain, and it is also uncertain whether CO₂ is reduced in small amounts to CO, or either of these gases direct to methane since the method of removing the products of the reaction by liquid air would not detect either methane or more CO. Harteck and Geib (unpublished experiments) have, however, observed that a mixture of CO and O_2 is in part oxidised to CO_2 when hydrogen atoms are brought into the mixture.

The reactions with halogens and the halogen hydrides have been examined in some detail. Unlike oxygen, chlorine and bromine react exceedingly quickly with hydrogen atoms, and indeed all hydrogen atoms have disappeared in 1/100 of a sec. This is readily understood since the reaction

$$\begin{array}{l} H + Cl_2 \rightarrow HCl + Cl + 44.5 \text{ Cals.} \\ H + Br_2 \rightarrow HBr + Br + 40.5 \text{ Cals.} \end{array}$$

³ Geib and Harteck, Z. physik. Chem., Bodensteinband 849, 1931; A. Farkas, Z. physik. Chem., 10B, 419, 1930. ⁴ See following paper, especially Geib and Harteck, Ber., 65, 1551 1932.

HYDROGEN ATOMS, OXYGEN ATOMS

are so strongly exothermic that reaction should follow at least every 10^4 collision. With chlorine, pure HCl is the product of the reaction, though with bromine the hydrogen bromide always contains some bromine, though there be a large excess of hydrogen atoms. The inference from this that there is some back reaction between HBr and H is strengthened by the fact that the forward reaction to produce HBr is much less than the theoretical amount arrived at from a knowledge of the actual concentration of hydrogen atoms.⁵ This back reaction has been directly observed by experiments in which HCl and HBr were mixed with H atoms, and in both cases reaction occurred instantaneously, *i.e.*, in less than 1/100 sec. and with a collision efficiency of more than I in 10,000. With HCl the gas is recovered unaltered as reaction product, while with HBr the HBr recovered contains some bromine. Thus the primary reactions are :—

and
$$\begin{array}{c} H + HCl \rightarrow H_2 + Cl + 0.5 \text{ Cals.} \\ H + HBr \rightarrow H_2 + Br + 16.5 \text{ Cals.} \end{array}$$

It is known that halogen atoms recombine rapidly on the walls, so that we must here assume that halogen molecules are formed from their atoms, which molecules then react again with hydrogen atoms to give halogen hydrides as described above. Iodine and hydrogen iodide behave in the same way as bromine and hydrogen bromide.

All hydrocarbons ⁶ are readily attacked by H-atoms with the production of methane which plays a unique part in these reactions. There are three possible modes of attack by the H-atom, all of which are actually found to occur. Firstly, there are addition reactions of the atom to radicals or unsaturated hydrocarbons which take place in the gas phase, or on the walls : also, since the CH linkage possesses an energy of about 90 Cals. and the CC link one of about 70 Cals., energetically the two other reactions, dehydrogenation, and the rupture of the carbon-carbon link in the hydrocarbon chain, are clearly possible.

The dehydrogenation process takes place with all hydrocarbons and their radicals by means of a series of steps :

$$C_n H_m + H \rightarrow C_n H_{m-1} + H_2.$$

The position of the CH radical in this scheme is perhaps uncertain; the energy of the binding in this radical is not known sufficiently exactly for it to be possible to conclude that the heat of dissociation is much more than 100 Cals., but if this is indeed the case it should not be possible further to dehydrogenate CH.

While the dehydrogenation of the higher hydrocarbons is fully established there is also the possibility of a rupture of the C—C link in hydrocarbons that have not been dehydrogenated. It is clear that this process takes place through a hydrogen atom coming into the place of a C—C linkage, thus producing from a saturated hydrocarbon another saturated hydrocarbon with fewer carbon atoms than the original, together with a free radical:

$$e.g., \qquad C_2H_6 + H \rightarrow CH_4 + CH_3.$$

This formulation is to be preferred to the other possibility

$$C_2H_6 + 2H \rightarrow 2CH_4$$

⁵ Cf. The determination of the H-atom concentration by Wrede and Harteck.

⁶ Bonhoeffer and Harteck, Z. physik. Chem., Haberband, 64, 1928, and von Wartenburg and Schultze, Z. physik. Chem., **2B**, 1, 1929.

P. HARTECK

since the latter requires three-body collisions and yet proceeds faster than such a process would allow. It is not possible to find a mechanism for the addition of hydrogen atoms causing hydrogenation in the gas phase which is not in disagreement with the known rate of dehydrogenation, and yet takes place through a three-body collision. One must either assume that the reaction takes place on the walls or that the addition of an atom of hydrogen to a radical which already contains a number of these atoms can indeed take place without the assistance of a third body.

Since these three reactions, hydrogenation, dehydrogenation and the breakdown of the carbon chain commonly take place simultaneously, in general a number of hydrogen atoms are required by a single molecule of hydrocarbon and the net result is similar to a catalytic union of hydrogen atoms with the molecule. It will be seen at once that the reaction involving the rupture of the chain is alone practically irreversible, and thus the products of the reaction will contain by far the greatest percentage of hydrocarbons containing fewer carbon atoms than the original material. Particularly remarkable is the stability of methane against hydrogen atoms.

The mono-halogen substitution products of methane react in less than 1/100 of a second with H-atoms (Boehm and Bonhoeffer, loc. cit.²). Methane and the hydrogen halide are the principal products, together with some ethane and free halogens in the cases of bromine and iodine. The primary reaction 7 must be

$$CH_3X + H \rightarrow CH_3 + HX.$$

Hydrogen sulphide is rapidly decomposed by hydrogen atoms with the deposition of sulphur. The energy of the two hydrogen sulphur linkages is together 171 Cals. and if it be correctly assumed that that of the first hydrogen linkage is not widely different from that of the second the reaction

$$H_2S + H \rightarrow H_2 + HS$$

is exothermic. The HS radical has then many possible modes of further reaction involving the separation of free sulphur.

Oxygen Atoms.

Oxygen atoms may be produced by means of a discharge tube in a manner similar to hydrogen atoms.⁸ In order to obtain high concentrations of oxygen atoms certain precautions must be taken which are not the same as those required to give high concentrations of hydrogen atoms, the main difference being due to an additional complication, the formation of ozone in the discharge tube, which often plays an important rôle. It is easy to show, by photographing the absorption of light of wavelength 2537 Å.U., that at room temperature the stationary concentration of ozone in the gas streaming from the discharge tube and containing a reasonable percentage of oxygen atoms lies in the neighbourhood of I per mille. If the effluent gas is cooled with solid carbon dioxide the concentration of ozone rises to 2 per cent., and if a gas, rich in oxygen atoms but containing no ozone at room temperature, is led through a

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⁷ Chadwell and Titani, J.A.C.S., 1933. ⁸ Weade Z. Physik. 54, 53, 1929. Harteck and Kopsch, Z. physik. Chem., 12B, 327, 1931.

vessel cooled in liquid air large amounts of ozone are collected in this vessel.

These results are in agreement with conceptions formed from work on the photo-chemical kinetics of the formation of ozone. If one assumes that the reaction $O + O_2 \rightarrow O_3$ takes place at every three-body collision, while the reaction $O+O_3\rightarrow 2O_2$ only takes place at every two thousandth collision between an atom of oxygen and a molecule of ozone, it is possible to calculate the stationary concentration of ozone that should exist under these conditions, which concentration is not greatly different from that found experimentally. That the efficiency of the decomposition reaction which is I in 2000 at room temperature decreases through the necessity for some energy of activation, is clearly shown by the increase in the concentration of ozone at low temperatures. These reactions of oxygen atoms are very clearly similar to those discussed in the section dealing with formation of hydrogen peroxide from oxygen and hydrogen atoms.

The reactions of oxygen atoms with hydrogen is by no means so high as might have been expected, and for example only one collision in 10⁷ between an atom of oxygen and a molecule of hydrogen is followed by reaction, the efficiency of this reaction being measured by a determination of the amount of water produced. As primary mechanisms of the formation of water the following reactions should be considered :---

(1) $H_2 + O \rightarrow OH + H + I$ Cal.

(2) $H_2 + O + M \rightarrow H_2O + 116$ Cals.

(3) $H_2 + 20 \rightarrow 20H + 103$ Cals.

the hydroxyl being then able to react further to give water according to the scheme $2OH \rightarrow H_2O + O$. In order to be able to select the correct mechanism from these possible ones, the dependence on temperature of the formation of the water has been examined experimentally, with the result that an energy of activation of about 6 Cals. was found to be required. From a knowledge of the lifetime of the oxygen atom in the experimental conditions it was found that every fourth three-body collision according to the scheme (2) or every tenth according to the scheme (3) would have to lead to reaction, and since an energy of activation of 6 Cals. implies that only every IO⁴ three-body collision is effective it must be concluded that if the reaction is indeed a homogeneous gas reaction, it must proceed according to scheme (1).

The reaction of oxygen atoms with water, according to the formulation $H_2O + O \rightarrow H_2 + O_2$ is only exothermic to the extent of 1.5 Cals. so that it is not to be expected that it would proceed any more readily than the inverse reaction, which certainly requires a very large energy of activation. In actual fact it is found that there is no reaction between water vapour and oxygen atoms. It may also be mentioned that the action of oxygen atoms on hydrogen, water, or other substances containing hydrogen, gave in no case a product in which hydrogen peroxide could be detected.

On the other hand, the hydrogen halides react relatively easily with atomic oxygen, about every 10^5 collision even with HCl leading to reaction. The action of O-atoms on HBr and HCl is so violent that a well-defined reaction zone is produced with a large increase in temperature which naturally leads to a marked increase in the velocity of the reaction. Certainly it is safe to say that every thousandth collision at the most is followed by reaction.

P. HARTECK

With ammonia oxygen atoms react at about every 10⁵th collision. As yet it is uncertain whether the atoms react to give water or the hydroxyl radical as primary product.

or (a)
$$\operatorname{NH}_3 + \operatorname{O} \to \operatorname{NH}_2 + \operatorname{OH}_2$$

(b) $\operatorname{NH}_3 + \operatorname{O} \to \operatorname{NH}_2 + \operatorname{H}_2\operatorname{O}_2$

Included in the reaction products besides water and nitrogen are a whole series of the oxidation products of ammonia.

The Hydroxyl Radical.

When substances containing hydrogen undergo combustion, certain bands and in particular a strong band at 3064, are observed in the emission spectrum which it is now certain are to be ascribed to the OH radical. The work of Hulthen and Zumstein 9 and more recently of Bonhoeffer and Reichardt ¹⁰ has proved that the OH radical in thermodynamic equilibrium with water vapour or mixtures containing the elements hydrogen and oxygen, at a temperature of 1500° C. or more is in a concentration large enough for its absorption spectrum to be Particularly in the work of the last authors are the final observed. doubts as to the nature of the radical dispelled. From the dependence of the concentration upon the temperature and the known heats of dissociation of hydrogen, oxygen, and water, the heat of formation H + O = OH can be calculated to be 102.7 Cals. Although our knowledge of the problem at high temperatures is fairly complete, we are relatively uninformed as to the lifetime and reactivity of this radical at room temperatures. So far it has not been possible to obtain the OH radical in sufficient concentration at room temperature for its absorption spectrum to be photographed. Bonhoeffer and Pearson¹¹ investigated the mechanism of the electrical discharge through water vapour at pressures of from 0.01 up to 3 mm. both spectroscopically by examination of the emission spectrum and by chemical observations. The lifetime of the OH radical produced in this way is very small (10⁻³ secs.) and so it is not possible to obtain higher concentrations.¹² The radicals are probably removed through the reaction $2OH = H_2O + O.^{13}$ In un published experiments, Geib and Harteck have found it impossible to detect the OH radical by absorption spectroscopy when it should have been produced by some chemical reaction at a pressure of about 0.7 mm. and in such conditions of streaming velocity (30 litres pro sec.) that the radicals could not have been lost by diffusion on to the wall. The reactions investigated were

$$O_3 + H = O_2 + OH$$
$$NO_2 + H = NO + OH$$
$$HBr + O = OH + Br$$
$$CO + O_2 + H = CO_2 + OH.$$

The radicals would have been easily detected in the absorption photographs had the concentration of the OH radical been only of the order of some hundredths of a mm. since a column of gas 40 cm. in length was used as light path. It was remarkable that no traces of hydrogen peroxide were ever detected in the products of any of these reactions.

⁹ Physic. Rev., 28, 13, 1926.

¹⁰ Z. physik. Chem., 139, 75, 1928.

¹¹ Ibid., 14B, 1, 1931.

12 Ibid., 139, 75, 1928.

¹³ For a more complete discussion of the possible modes of removal of OH, cf. Bonhoeffer and Pearson, loc. cit. (11).

HYDROGEN ATOMS, OXYGEN ATOMS 140

It is thus clear that the lifetime of the OH radical is much less than that of hydrogen and oxygen atoms, and that there is little possibility of studying its reactions without the presence of secondary reactions. Its detection is rendered specially difficult through the fact that hydrogen atoms in the presence of molecular oxygen will start such oxidation reactions as had been held to indicate the presence of OH.

None the less, the OH radical is of great importance in modern theories of reaction kinetics, in which it is often an important member of a reaction chain,¹⁴ more especially at temperatures of some hundred degrees.

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14 Cf. Haber and co-workers in the Kaiser Wilhelm Institut für physikalisch Chemie.