THE ADDITION REACTIONS OF HYDROGEN AND OXYGEN ATOMS AT LOW TEMPERATURES.

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Atoms of oxygen and hydrogen, produced in a discharge at a pressure of $\frac{1}{2}$ mm. of mercury, rarely react at room or higher temperatures to give addition products. At low pressures the formation of such addition products is hindered by the greater chance of a successful exchange reaction, and such products as are formed are forthwith decomposed as, for example :

1. $A + B + M = AB + M$ but AB is decomposed,
2. $AB + A = A_2 + B$,

where A is the atom under consideration, B any reagent, and M the requisite third body. Since such exchanges, even with atoms giving rise to exothermic reactions, require in most cases an activation energy of some Cals, it must be possible by decreasing the temperature of the reaction vessel to suppress the decomposition reaction and thus to obtain those addition products formed without any heat of activation, free from secondary products.

In our experiments, the oxygen or hydrogen atoms were mixed with the different gases at the low temperature; or when the reagent had an inappreciable vapour pressure, it was brought into the reaction vessel and mixed with the atoms before being condensed, being led to the middle of the cooled reaction vessel by the help of a warmed double walled tube. We have already described the formation of H_2O_2 [1] in this way by the addition of two atoms of hydrogen to a molecule of oxygen at the temperatures of liquid air or liquid hydrogen. This reaction has no measurable heat of activation, and certainly takes place in two stages,

the first $\quad O_2 + H + M \text{ (or wall)} = HO_2 + M$
and $\quad HO_2 + H + M \text{ (or wall)} = H_2O_2 + M.$

It was not possible to freeze out HO_2 even with the help of liquid hydrogen in the presence of a large excess of oxygen. At the temperature of liquid hydrogen it was possible to obtain a 100 per cent. yield of H_2O_2, but this was not of the normal form, though it changed to the usual form on warming to — 80° C., at which temperature there was some decomposition into water and oxygen and considerable foaming.

At low temperatures, mercury vapour with H atoms gave a solid body [1] containing 70 per cent. HgH. H atoms with NO at the temperature of liquid air gave a body [2] of the composition $(HNO)_n$ which was a very explosive substance, but which on cautious warming gave hyponitrous acid and nitramide, while undergoing some decomposition to N_2O and H_2O. Carbon monoxide does not react with H atoms at low temperatures. At room temperatures the reaction can be followed by subsequently freezing out the products, and in these conditions Bonhoeffer and Boehm [3] obtained traces of formaldehyde. It is well known that H atoms produced photochemically with mercury as a sensitiser produce formaldehyde and other aldehydes with a quantum efficiency of about 1.[4] Thus it is clear that the reaction $H + CO + M = COH + M$ has an energy of activation, so that it cannot proceed at low temperatures, but goes readily at the temperature of the room; and it has been calculated that this energy must be between 3 and 7 Cals.

In the reaction with HCN at low temperatures we obtained a substance having the composition H_3CN, which on slow heating broke down into known substances, methylamine, ammonia and a series of condensation products, while some HCN was reformed.

$$\left.\begin{aligned} HCN + H + M &= H_2CN + M \\ H_2CN + H + M &= H_3CN + M \end{aligned}\right\} \text{Low temperature.}$$
$$2H_3CN = HCN + CH_3NH_2 \text{ on warming.}$$

An actual yield of some 33 per cent. of methylamine was obtained. It appears therefore that at low temperatures the nitrogen behaves as though it were quinquevalent.

[1] K. H. Geib and P. Harteck, *Ber.*, **65**, 1551, 1932.
[2] P. Harteck, *Ber.*, **66**, 423, 1933.
[3] *Z. physik. Chem.*, **119**, 385, 1926.
[4] W. Frankenburger, *Z. Elektrochem.*, **36**, 757, 1930.

On the other hand ammonia and methylamine do not react directly with hydrogen atoms under these conditions. Sulphur dioxide gave an addition product whose composition can be represented as H_2SO_2, which decomposed when the temperature was raised to give H_2S and SO_2, and also some H_2O and sulphur.

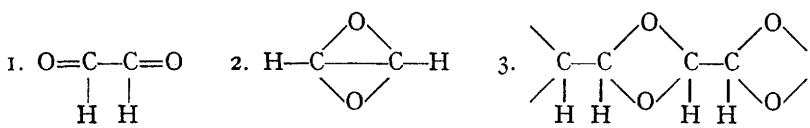
Benzene gave a hydrogenation product which by analysis had a net composition of 17 per cent. dihydrobenzene. Ethylene was reduced and gave a 30 per cent. yield of ethane. With our apparatus we were able to obtain no less than half a litre of ethane at atmospheric pressure in fifteen minutes, so that in this and indeed in all the other experiments, no difficulty was experienced in identifying the products.

It is clear that there are many other gas reactions in which addition products with hydrogen atoms can readily be obtained. Likewise, oxygen atoms may be shown to give many addition products, of which some are discussed below.

In all experiments with oxygen atoms, the reaction vessel was cooled with liquid oxygen rather than with liquid air, for otherwise large amounts of ozone are formed and condensed, which, in the presence of organic bodies, is exceedingly dangerous. The boiling-point of oxygen is some 8° higher than that of liquid air, and this difference is sufficient to suppress the formation of ozone in our apparatus. The formation of ozone itself is an addition reaction of the type under consideration.[5]

With oxygen atoms, ethylene gave a colourless product which at — 110° began to undergo molecular rearrangement. At room temperature, ethylene oxide, acetaldehyde, formaldehyde, carbon monoxide, and condensation products of aldehyde were formed.

Acetylene readily gives addition products with oxygen atoms. A large amount of glyoxal is found, but other reaction products are so unstable that they are decomposed at the temperature of liquid air with the production of CO. From the yield obtained it was found that one molecule of acetylene requires two atoms of oxygen, and it may be that one oxygen atom is bound only to one carbon atom, or to two carbon atoms from the same or different molecules.



1 is glyoxal, the others, 2 and 3, give rise to the decomposition products which accompany it. It may be mentioned that formic acid is found as well as water, carbon monoxide and carbon dioxide.

Benzene with oxygen atoms at the temperature of liquid air gives but 10 per cent. of addition product, but when the reaction vessel was merely cooled with acetone and CO_2 to — 80° all the benzene was attacked and changed to a colourless glassy solid, which began to decompose at — 30° into stable products. Combustion gave $C_6H_6O_{3\cdot5}$ as its composition. Since the reaction proceeds practically quantitatively at — 80° while at — 170° it is very much suppressed, it may be calculated that the heat of activation is roughly 2 Cals.

Carbon monoxide gave 1·3 per cent. carbon dioxide, *i.e.*, about the

[5] Harteck and Kopsch, *Z. physik. Chem.*, **12B**, 327, 1931.

same amount as at room temperature.[6] Sulphur dioxide gave under the same conditions about 8 per cent. SO_3. HCl is oxidised to ClO_2 to the extent of about 5 per cent.

The interaction of oxygen and hydrogen atoms with various gaseous substances at low temperatures gives rise in many cases to addition products, which are only stable at low temperatures, but which on warming slowly change to known substances. As a preliminary to these processes, the breaking of a double bond, or the changing of an atom to a higher valency, is necessary. The heat of activation for such reactions are often immeasurably small.

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[6] *Cf.* Harteck and Kopsch, *loc. cit.* 51.