THE PHOTOSENSITISED FORMATION OF HYDROGEN PEROXIDE IN THE SYSTEM HYDROGEN-OXYGEN CHLORINE.

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The part played by oxygen in reducing the speed of the photochemical reaction between hydrogen and chlorine has been interpreted in various ways. The general kinetics of the reaction indicate that (when oxygen is present) the velocity is approximately inversely proportional to the pressure of oxygen, and it may be deduced that practically all the reaction chains are terminated through the agency of an oxygen molecule. On the basis of the "energy chain" mechanism supported by earlier workers[1] this action was supposed to consist in a deactivation of the energy-rich chlorine or hydrogen chloride molecules by collisions of the second kind

$$Cl_2^* + O_2 = Cl_2 + O_2^*$$
$$HCl^* + O_2 = HCl + O_2^*$$

but the explanation suffers from the disadvantage that oxygen has practically no effect on the somewhat analogous photo-synthesis of phosgene. We shall not pursue it further since for other well-known reasons, both spectroscopic and kinetic[2] it may be held that the "energy chain" must now be replaced by a mechanism involving propagation by chlorine and hydrogen atoms, after the scheme first suggested by Nernst.[3] In this, the primary act of the light is to dissociate the chlorine molecule into atoms

$$Cl_2 = Cl + Cl'$$

of which one atom is in the metastable $2P_1$ state.[4] A feature of the later views of this mechanism is that the chain is only propagated by the excited chlorine atom, which alone is deemed able to dissociate the hydrogen molecule

$$Cl' + H_2 = HCl + H.$$

The reaction chain is then continued by

$$H + Cl_2 = HCl + Cl'$$

and these phases are repeated indefinitely.

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[1] Bodenstein, *Z. Electrochem.*, **22**, 58, 1916; Chapman, *J.C.S.*, **123**, 3079, 1923; Thon, *Fortschr. Chem.*, **18**, Heft 11, 1926.

[2] Franck, *Trans. Farad. Soc.*, **21**, 536, 1926; Kuhn, *Z. Physik*, **39**, 77, 1927; Rollefson, *J. Amer. Chem. Soc.*, **51**, 770, 1929.

[3] Nernst, *Z. Electrochem.*, **22**, 62, 1916.

[4] Kuhn, *loc. cit.*, 2.

According to Cremer,[5] the effect of oxygen in reducing the speed is explained by its deactivating effect on the excited chlorine atoms,

$$Cl' + O_2 = Cl + O_2'$$

which are thereby rendered incapable of reacting with hydrogen. It is known that the oxygen simultaneously reacts to form water,[6] and this has been represented as a reaction between the excited oxygen molecules produced as above, and hydrogen molecules according to the equation proposed by Cremer

$$O_2' + 2H_2 = 2H_2O.$$

Quite apart from kinetic difficulties, it would seem, however, very doubtful whether this mechanism can be admitted, since the low energy of activation of the metastable chlorine atom (0·109 volt), is certainly insufficient to activate the oxygen molecule to the point of reaction with hydrogen.

Further, any chemical process involving the removal of chlorine atoms by reaction with oxygen to form for example ClO_2 suffers from the difficulty, among others, that it should involve a similar retardation of the phosgene synthesis, by oxygen, which as already stated is not observed, nor has any such oxygenated product of chlorine ever been observed. We shall therefore propose that oxygen acts, not by deactivation of or reaction with chlorine atoms, *but solely by reaction with the hydrogen atoms propagating the reaction chains.*

The matter is now made much clearer by the work of Haber and his school[7] on the homogeneous reaction between hydrogen and oxygen. They give strong evidence, based upon a spectroscopic study of the hydrogen-oxygen flame, that the reaction is propagated by chains involving free hydroxyl radicles, according to the scheme

$$H + H_2 + O_2 = HO + H_2O \quad . \quad . \quad . \quad (a)$$
$$HO + H_2 = H + H_2O. \quad . \quad . \quad . \quad . \quad (b)$$

Below 400° C. which is the lowest temperature of explosion, reaction (*b*) requires activation and cannot proceed spontaneously, so that the chain mechanism can no longer occur. Instead, the free hydroxyl radicles may unite to form hydrogen peroxide and this can be isolated,—for example by playing the flame on a cold surface such as solid carbon dioxide.

These results would seem to give us the key to the action of oxygen in the hydrogen chlorine reaction. The free hydrogen atoms propagating the hydrogen-chlorine chains will also react according to equation (*a*) above; but since reaction (*b*) cannot follow at ordinary temperatures there should be an accumulation of hydrogen peroxide in the system. In confirmation of this view we may cite the experiments of Marshall[8] in which hydrogen peroxide in considerable quantities was produced in mixtures of hydrogen and oxygen by the photosensitising action of mercury vapour in light of wavelength 2536 ÅU. In this case, there is little doubt that the first phase of the reaction is the liberation of hydrogen atoms, and quantitative evidence for the scheme

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[5] Cremer, *Z. physikal. Chem.*, **128**, 285, 1927.

[6] Weigert, *Ann. Physik*, **24**, 243, 1907; Norrish and Rideal, *J.C.S.*, **127**, 790, 1925; Cremer, *loc. cit.*, 5.

[7] Bonhoeffer and Haber, *Z. physikal. Chem.*, **A 137**, 263, 1928; Farkas, Haber and Harteck, *Naturw.*, **19**, 266, 1930.

[8] Marshall, *J. Amer. Chem. Soc.*, **49**, 2763, 1927.

$$Hg^* + H_2 = H + H + Hg$$
$$H + O_2 + H_2 = HO + H_2O$$
$$HO + HO + M = H_2O_2$$

has recently been adduced by Klinkhardt and Frankenburger.[9]

It therefore seemed probable that hydrogen peroxide as well as water is also a product in the hydrogen-chlorine reaction when oxygen is present, and this has been tested and fully confirmed in the following experiments.

Experimental.

(*a*) Hydrogen (250 mm.), oxygen (250 mm.), and chlorine (150 mm.) were enclosed in a spherical reaction vessel of about 250 c.c. capacity. Attached to the reaction vessel was a side tube with a stopcock through which a small quantity (5 c.c.) of water could be rapidly introduced. The reaction vessel was attached to a glass Bourdon gauge sensitive to small pressure changes of 0·002 mm., and kept at a constant temperature by immersion in a bath of water. The vessel and contents were irradiated for 80 minutes by a mercury vapour lamp, using glass lenses so that no light of wavelength less than 3500 ÅU entered the system. During this time the pressure fell by some 2 mm., corresponding to a formation of about 6 mm. of water vapour, according to the equation

$$2H_2 + O_2 = 2H_2O.$$

At the end of this period the water was introduced through the side arm, and the light was simultaneously shut off. After standing for 5 minutes the reaction vessel was removed, and the resulting solution of chlorine and hydrogen chloride tested for the presence of hydrogen peroxide with a solution of titanic acid. A clear positive result was obtained while control experiments using chlorine water and hydrogen chloride mixtures alone gave absolutely no effect. Comparison of the yellow colour obtained against that given by a standard solution of hydrogen peroxide indicated, however, that only a relatively small quantity of hydrogen peroxide was present, corresponding to a pressure of ·02 mm. in the original reaction vessel. The smallness of this quantity compared with the total water formation of 6 mm., suggests that the hydrogen peroxide was destroyed by the light almost as fast as it was formed, so that a photostationary state involving only a small concentration resulted. This point was confirmed by the following experiment:

(*b*) Approximately equal currents of hydrogen, chlorine and oxygen from cylinders, after bubbling through water and subsequent drying by calcium chloride and phosphorus pentoxide, were mixed, and rapidly streamed through a water jacketed glass tube, which was subjected to the light of two mercury vapour lamps. The outgoing gases containing hydrogen chloride, water, and hydrogen peroxide, were passed through 50 c.c. of water in a wash bottle which was kept screened from the light. The apparatus was made of glass throughout. After the gases had been streaming for about half an hour, the chlorine was shut off, and the dissolved chlorine displaced from the water in the wash bottle by a stream of hydrogen and oxygen. The solution was then tested with titanic acid, and gave a strong positive reaction for hydrogen peroxide. In a second experiment, in which the gases were passed for two hours, the hydrogen peroxide collected, after

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[9] Klinkhardt and Frankenburger, *Z. physikal. Chem.*, **B 8**, 138, 1930.

diluting to five times the volume, was estimated colorimetrically with titanic acid against a standard solution. The amount collected was in this way found to be 0·0026 gms., a quantity equivalent to about 1·5 c.c. of $N/10$ H_2O_2 solution.

Control experiments using a similar gas stream without the light, and also a stream of hydrogen and oxygen only with the light on, indicated no trace of hydrogen peroxide. It is therefore clear that hydrogen peroxide in considerable quantities can be isolated when hydrogen, chlorine and oxygen are illuminated with visible and long wave ultra-violet light, provided precautions are taken to remove the products as rapidly as possible from the decomposing action of the light.

Conclusions.

These facts taken in conjunction with those cited above, make it probable that the action of oxygen in inhibiting the hydrogen chlorine reaction, lies in its reaction with the hydrogen atoms, according to the scheme

$$\begin{aligned} H + H_2 + O_2 &= H_2O + OH \\ OH + OH + X &= H_2O_2 + X'. \end{aligned}$$

By this process both water and hydrogen peroxide are formed. It follows further that the OH radicle cannot participate in the hydrogen chlorine chain as postulated by Coehn and Jung[10] and therefore rules out the possibility of accounting for the catalytic action of water on such a basis. The author has pleasure in expressing his indebtedness to Dr. J. G. A. Griffiths for assistance with some of the experimental work recorded above.

Summary.

Reasons are given for supposing that the inhibiting action of oxygen in the photochemical reaction between hydrogen and chlorine is due solely to reaction of the oxygen molecules with the hydrogen atoms of the chains, with the formation of free hydroxyl radicles. On the basis of the recent work of Haber and others on the mechanism of the homogeneous reaction between hydrogen and oxygen, these hydroxyl radicles should combine at room temperature to give hydrogen peroxide. In confirmation of the above hypothesis, the production of hydrogen peroxide in appreciable quantities when mixtures of hydrogen, chlorine and oxygen, at atmospheric pressure are irradiated in glass apparatus by a mercury lamp has been demonstrated.

[10] Coehn and Jung, *Ber.*, **56B**, 696, 1923.

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