

185. *The Photochemical Union of Chlorine and Hydrogen in the Presence of Oxygen, and the Relative Rates of Formation of Water and Hydrogen Chloride in Illuminated Mixtures of the Three Gases Rich in Oxygen.*

By DAVID L. CHAPMAN and JOHN S. WATKINS.

IN 1913 Chapman and Underhill (J., **103**, 496) observed that hydrogen has an inhibitive effect on the rate of photochemical union of chlorine and hydrogen when oxygen is present in the mixture and the partial pressure of the hydrogen exceeds a given value. The result was confirmed by Jones and by M. C. C. Chapman (J., **1923**, **123**, 3062), who also showed that the inhibitive effect of oxygen is inappreciable when the pressure of the hydrogen is very low. Bearing on this question are some results recently obtained by Gibbs (*Nature*, 1931, **127**, 854) which have not yet been published in detail. These have shown that when specially purified moist chlorine and hydrogen (the latter gas being at a low pressure) are exposed to light, the rate of formation of hydrogen chloride is proportional to the square root of the intensity of the light* and is not affected by the addition of small amounts of oxygen.

Mrs. Chapman's results were expressed by the formula

$$d[\text{HCl}]/dt = k_1 I [\text{Cl}_2]^2 [\text{H}_2] / \{k_2 [\text{H}_2]^{2-x} [\text{O}_2] + [\text{Cl}_2]\}$$

in which I is the intensity of the light and x is a number between 0 and $\frac{1}{2}$. The formula expresses the fact that hydrogen can become an inhibitor and that oxygen can cease to be an inhibitor when the pressure of the hydrogen is low. It was, however, deduced on the assumption that the photochemical change in question obeys in all circumstances Draper's law and will therefore need modification; this is not discussed at present.

Thon (*Z. physikal. Chem.*, 1926, **124**, 332) contests Underhill's results, and modifies Mrs. Chapman's formula to one of a similar character which, however, does not indicate that oxygen practically ceases to act as an inhibitor when the concentration of the hydrogen is low, or that hydrogen can act as an inhibitor. Bodenstein and Schenk (*ibid.*, 1933, **B**, **20**, 420) refer to Thon's formula as "Das Gesetz, das sich insbesondere in den sehr exakten Messungen von Thon äusserst bestimmt bewährt hat," and base a theory concerning the simultaneous photochemical formation of water and hydrogen chloride from a mixture of the elements on the law. To this theory we shall refer later.

Mrs. Chapman at the end of her paper stated that her results could be explained with appropriate assumptions by Nernst's theory. The suitable assumptions were not given. They concerned the mechanism of the formation of water, about which very little was known, and might at the time have been considered fanciful. However, in the meantime, through the researches of Taylor, Hinshelwood, Marshall and Bates, Haber, Frankenburg, Bonhoeffer, and others, sufficient is now known about the interaction of hydrogen and oxygen to justify speculation concerning the mode of formation of water in an illuminated mixture of hydrogen, oxygen, and chlorine. Let us see which of the theories proposed by the above investigators will explain Underhill's and Chapman's results.

* This result was predicted by Berthoud, who was the first to demonstrate clearly that photochemical changes can be proportional to the square root of the intensity of the light.

A Nernst scheme which will account for the inhibitive effect of oxygen is :



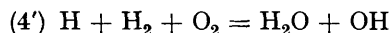
If it be assumed that the last reaction is not reversible, and that the hypothetical compound HO_2 decomposes without interaction with any of the atoms or molecules present in the reacting mixture, it is obvious that the amount of hydrogen which combines with oxygen in the most favourable circumstances should not exceed that which combines with chlorine. Since our results show, however, that the former *can* exceed the latter, the simple scheme proposed above is incorrect.

Moreover, the following differential equation can be derived from the proposed scheme :

$$d[\text{HCl}]/dt = 2(k_1k_3/k_4)I[\text{Cl}_2]^2/[\text{O}_2] + k_1I[\text{Cl}_2] \dots \dots (1)$$

which is incompatible with both Underhill's and Mrs. Chapman's results.

If, however, we replace equation (4) in the above scheme by the more probable equation



and assume with Haber that the neutral hydroxyl cannot interact with molecules of hydrogen at the temperature of the experiment to regenerate atoms of hydrogen, then the hydrogen which combines with oxygen can exceed that which combines with chlorine, in agreement with the results of our experiments.

Again, from the scheme thus modified the following differential equation can be deduced :

$$\frac{d[\text{HCl}]}{dt} = \frac{2k_1k_3}{k'_4} \frac{I[\text{Cl}_2]^2}{[\text{H}_2][\text{O}_2]} + k_1I[\text{Cl}_2] \dots \dots (2)$$

making both hydrogen and oxygen inhibitors, in agreement with Underhill's and Mrs. Chapman's results at moderate concentrations of hydrogen and oxygen.

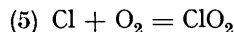
There is an apparent paradox in equations (1) and (2). Equation (1) makes the rate of formation of hydrogen chloride independent of the concentration of the hydrogen at all concentrations of that element, and according to equation (2) the rate of formation of hydrogen chloride becomes infinitely great when the concentration of the hydrogen is infinitely small. The apparent paradox is due to the neglect to take into account the effects of homogeneous and heterogeneous recombination of the atoms and other causes of retardation in deducing the formulæ.

There are other modifications of the Nernst scheme which will account approximately for the results of Underhill, Mrs. Chapman, and ourselves. The consideration of these will be omitted, as we think that in the present state of our knowledge an exhaustive examination of all the possibilities would be tedious and unprofitable. We must, however, consider briefly the paper of Bodenstein and Schenk mentioned above, and draw attention to an argument contained therein which appears to be inconclusive.

Thon's formula, which, as the authors state correctly, does not indicate a trace of inhibition by hydrogen, chlorine, or hydrogen chloride, is : *

$$\frac{d[\text{HCl}]}{dt} = \frac{4J_{\text{abs.}}k_3[\text{H}_2][\text{Cl}_2]}{k_4[\text{O}_2]\{[\text{H}_2] + k_3k_5[\text{Cl}_2]/k_2k_4\}}$$

and follows with legitimate approximations from the Nernst scheme as above with the addition of



Bodenstein and Schenk, having modified (4) and (5) so as to include the third molecule, M, required to stabilise the products HO_2 and ClO_2 (M being a molecule of any one of the interacting gases chlorine, hydrogen chloride, or hydrogen, each of which is assumed to be equally effective as a "third body"), make the necessary correction in Thon's formula and write it

$$\frac{d[\text{HCl}]}{dt} = \frac{4J_{\text{abs.}}k_3[\text{H}_2][\text{Cl}_2]}{k_4[\text{O}_2]M\{[\text{H}_2] + k_3k_5[\text{Cl}_2]/k_2k_4\}}$$

* We have corrected an obvious misprint in the text of their paper.

But owing to the equal effectiveness of molecules H_2 , Cl_2 , and HCl as "third bodies," M stands for $[H_2] + [HCl] + [Cl_2]$, and the modified formula indicates that there can be inhibition by both hydrogen and hydrogen chloride.* In other words, Bodenstein and Schenk's modified formula and Thon's formula are inconsistent unless the k_4 and k_5 of the latter are not true velocity constants of chemical reaction but merely quantities which remain constant under conditions restricting the concentrations of the gases in the system.

We raise no objection to the modified formula provided that it be admitted that (1) Thon's method of investigation was incapable of demonstrating whether there was or was not an inhibition by hydrogen or hydrogen chloride, (2) the formula is not applicable to the range of concentrations where oxygen practically ceases to act as an inhibitor.

Researches on the subject of this communication have been published by Weigert (*Ann. Physik*, 1907, **24**, 253), who discovered that water is formed when a mixture of hydrogen, chlorine, and oxygen is exposed to light; Norrish and Rideal (J., 1925, **127**, 787); Cremer (*Z. physikal. Chem.*, 1927, **128**, 285), and Bodenstein and Schenk (*loc. cit.*). Norrish (*Trans. Faraday Soc.*, 1931, **27**, 461) has shown that hydrogen peroxide is one of the products of the photochemical interaction of hydrogen, chlorine, and oxygen.

Our aim has been, as stated above, to determine the highest attainable ratio of the number of water molecules to those of hydrogen chloride, and we have shown that this ratio can exceed 0.5. We are unable to say whether the ratio approaches a fixed number asymptotically. This question could probably only be decided by performing experiments with mixtures at pressures considerably above that of an atmosphere, and in such circumstances the analyses would present considerable difficulties. The result we have obtained is in theoretical agreement with the fact that the molecules of water produced per quantum can rise as high as 2, and can therefore be regarded as giving support to the interpretation of the latter fact.

EXPERIMENTAL.

The all-glass apparatus consisted of two glass containers of unequal capacity which could be brought into communication by opening a tap. Generally, the capacity of one container was not more than 3 c.c. and that of the other not less than 70 c.c. To perform an expt., the smaller container was filled with dry Cl at a recorded temp. and press., and the larger with a dry mixture of H and O . The intercommunication tap was then opened, and the gases allowed to mix in the dark. The apparatus was exposed to sunlight for at least 12 hr. Sunlight was more effective than that of a 1000-watt W -filament lamp. After the illumination, the total vol. of H and O contained in the apparatus was determined by gas analysis, and the HCl and uncombined Cl_2 estimated in the usual way with 0.01*N*- I aq. The ratio $\frac{H \text{ combined with } O}{H \text{ combined with } Cl}$

i.e., $\frac{2 \times \text{mols. of } H_2O \text{ formed}}{\text{mols. of } HCl \text{ formed}}$, calculated from the Cl taken and Cl uncombined and the contraction of the total vol. of H and O reduced to *N.T.P.*, is given in the last column of the following table, in which all quantities (except the ratio) represent millimols.

$H_2 + O_2$ taken.	$H_2 + O_2$ found.	Cl_2 taken.	Cl_2 found.	$\frac{2 \times H_2O}{HCl}$	$H_2 + O_2$ taken.	$H_2 + O_2$ found.	Cl_2 taken.	Cl_2 found.	$\frac{2 \times H_2O}{HCl}$
Ratio $H_2 : O_2 = 2 : 1$.									
4.238	2.327	1.191	0.025	0.43	3.320	3.170	0.0861	0.0045	0.55
4.215	2.923	1.184	0.175	0.12					
Ratio $H_2 : O_2 = 1 : 2$.									
8.330	7.879	0.1227	0.0025	1.83	6.073	5.974	0.0314	0.0001	1.55
8.258	7.877	0.1216	0.0015	1.45	8.802	8.576	0.0629	0.0017	1.68
6.189	5.909	0.0775	0.0025	1.81	8.445	8.183	0.0893	0.0015	1.39
6.680	6.512	0.0482	0.0008	1.71					

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* According to this formula, if the concentrations of the chlorine and hydrogen chloride are kept constant, a maximum rate of combination occurs when $[H_2] = 0.317[Cl_2]$, it being assumed that $k_3k_5/k_2k_4 = 0.1$ as found by Thon at atmospheric pressure. Mrs. Chapman found a maximum rate when the concentration of the hydrogen was between 0.20 and 0.25 that of the chlorine.