

published data on separation by electrolysis and of desorption with the consequent necessity for different velocities of desorption, and therefore of adsorption, of isotopes at electrode surfaces was also realized by Professor Hugh S. Taylor who is arranging for an experimental test of the possibilities of separation by such processes.

¹ E. W. Washburn and H. C. Urey, *Proc. Nat. Acad. Sci.*, **18**, 496 (1932).

² H. Eyring and M. Polanyi, *Z. physik. Chem.*, [B] **12**, 279 (1931).

³ A. Sherman and H. Eyring, *J. Am. Chem. Soc.*, **54**, 2661 (1932).

⁴ R. W. Gurney, *Proc. Roy. Soc. (London)*, **A134**, 137 (1931).

THE REACTION OF HYDROGEN ATOMS WITH OXYGEN AND THE HYDROGEN CHLORINE REACTION

BY JOHN R. BATES

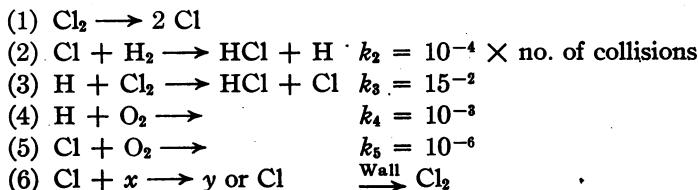
DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MICHIGAN

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The rapidity with which the experimental facts connected with the photochemical union of hydrogen and chlorine change and have changed during the last century, always gives a discouraging outlook to any complete solution of the mechanism of the reaction. The results obtained during the last year, however, while still representing a comparative mobile condition, tend for the most part toward a greater simplification of the problem.

Notable among these results is the discovery in Bodenstein's laboratory^{1,2} that the influence of water vapor on the reaction is not as given by the earlier work of Coehn and Jung. It is found that water vapor is without effect on the reaction. Thus is removed a difficulty which seemed to be increasingly impossible of explanation, in spite of a number of ingenious attempts.

At the symposium on photochemistry held by the Faraday Society³ in 1931, Bodenstein pointed out that many of the facts of the reaction could be correlated in a very simple manner if we postulate the following mechanism:



From these may be derived the equations representing the experimental results of Thon,⁴

$$\frac{d [HCl]}{dt} = \frac{4 k_2 k_3 I \text{ abs } [H_2] [Cl_2]}{OH (k_2 k_4 [H_2] + K_3 K_5 [Cl_2])} \quad (1)$$

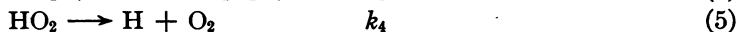
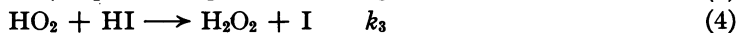
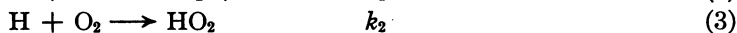
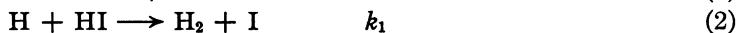
in the case where there is oxygen present in the reaction system. In oxygen-free gases, we obtain

$$\frac{d [HCl]}{dt} = \frac{4 k_2 I \text{ abs } [H_2]}{k_6 [x]} \quad (2)$$

the results of Bodenstein and Unger.⁵ Bodenstein then went on to evaluate the most probable values for the constants of the various reactions. From certain considerations, such as the fact that oxygen does not appreciably alter the combination of hydrogen and bromine and that the ratio of k_3 to k_4 must be about 20:1 as given by Cremer,⁶ he arrives at the values of the efficiencies of these reactions given above.

He then showed that, while this scheme gives an excellent description of many of the experimental facts, there were several considerations which stood in the way of an acceptance of this mechanism as a complete picture of the reaction. One of these, the influence of water vapor on the reaction, has been removed by him as already stated. A second, the change in quantum efficiency with wave-length as reported by Allmand, seems now to be better understood in the light of the recent work of Ritchie and Norrish.⁷ These authors find that hydrogen chloride has an inhibiting effect on the reaction, and suggest that it was this which caused the anomalous results reported by Allmand. A third difficulty which stood in the way of a complete acceptance of this mechanism was that reaction (4) was written in a bimolecular form but should, since it is an association reaction, involve the presence of a third body. It is the purpose of this paper to show how this third difficulty is removed by the results obtained by Dr. Lavin⁸ and the author from the photooxidation of hydrogen iodide. And in addition the value of $k_4 = 10^{-3} \times \text{no. of collisions}$ deduced by Bodenstein, is obtained from entirely independent experimental data.

According to the most generally accepted theories the mechanism of the photooxidation of hydrogen iodide may be presented by the scheme:

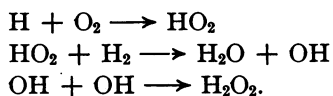


The hydrogen iodide is decomposed into atoms by the action of light. The hydrogen atom so produced has two courses which it may follow. It may react with a second hydrogen iodide molecule according to (2). This is the reaction which takes place in the straight decomposition of

hydrogen iodide by light. The atom may also unite with oxygen according to (3), producing an energy rich HO_2 molecule. This molecule may then react on collision with another hydrogen iodide molecule as in (4), if it will remain stable sufficiently long. It may dissociate spontaneously (having its energy of formation still contained in the molecule) as in (5). The mean lifetime of the HO_2 molecule is given by the reciprocal of k_4 . Our k_2 here is obviously Bodenstein's k_4 of the hydrogen chlorine reaction. It is upon the magnitude of the lifetime of HO_2 that the assumption made by Bodenstein, namely that the reaction of hydrogen atoms with oxygen is bimolecular, depends. If the HO_2 molecule may remain undecomposed for a sufficiently long time, the reaction is bimolecular; if dissociation occurs very rapidly, the reaction is then termolecular. A bimolecular reaction may thus be postulated if we may neglect entirely reaction (5). This is what Bodenstein has done. Experimentally this is shown to be completely justified by the work of Lavin and Bates, to which reference has already been made. This comes about from the fact that the kinetic expression which is found to represent this reaction does not involve k_4 . Furthermore, the relative efficiency of the reaction of hydrogen atoms with hydrogen iodide and with oxygen is found to be 10:1 ($k_1/k_2 = 10$). The reaction of hydrogen atoms with hydrogen iodide is known to take place once in every 100 collisions. Hence the reaction $\text{H} + \text{O}_2$ takes place bimolecularly and once in every 1000 collisions, exactly as postulated by Bodenstein.

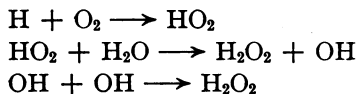
His keen analysis of the hydrogen chlorine reaction has also had support in the recent work of Rodebush and Klingelhoefer on the collision efficiency of the reaction $\text{Cl} + \text{H}_2$. It is found that this reaction goes in one every 10^6 collisions, whereas the value suggested by Bodenstein was 10^4 .

The data which have accumulated in connection with the reaction do not, however, contain purely unmitigated blessings. The fact that hydrogen chloride inhibits the reaction will have to be taken into account. In addition, the work of Salley and Bates would seem to make necessary a reconsideration of the manner in which the chains of the hydrogen chlorine reaction are broken by oxygen. The chain breaking property of oxygen is usually explained by the mechanism of the reaction of hydrogen atoms with oxygen proposed by Haber:



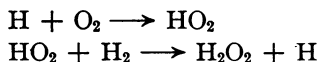
In this representation of the reaction the hydrogen chlorine chains are cut off short by the disappearance of a hydrogen atom accompanied by the formation of one molecule of water and one half molecule of hydrogen peroxide. However, Salley and Bates⁹ have demonstrated that,

with hydrogen atoms produced by excited mercury atoms, it is possible to obtain 90% hydrogen peroxide in the reaction of these atoms with oxygen, a result quite incompatible with such a mechanism. They further tested an alternative process

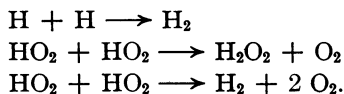


suggested by Frankenburger and Klinkhart¹⁰ and showed that if these two processes could account for the high peroxide product in dry gases the reaction of HO_2 with H_2O would have to go at least 5×10^3 times as fast as the reaction of HO_2 with H_2 . This would mean that if this mechanism represented the true state of affairs, small amounts of water would exert an inhibiting effect on the hydrogen chlorine reaction in the presence of oxygen. There is apparently no experimental evidence on this point.

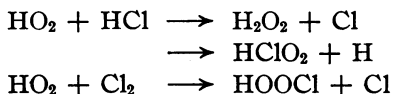
But, in addition, it was shown that the water vapor concentration was without the effect on hydrogen peroxide formation which should be expected from this mechanism. The suggestion was made that the reaction might perhaps be better represented by the mechanism suggested by Taylor and Marshall:



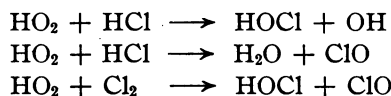
with the possible reactions ending the chains:



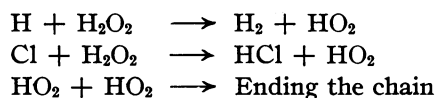
The chief objection to such a mechanism is the shortness of the chains involved in the reaction, as determined experimentally. (1-2.) This, however, does not make this process impossible, but shows that, if it be the correct one, the chain breaking reactions must take place with greater rapidity than the chain propagating reactions. Be that as it may, these results give room for considerable conjecture on how the hydrogen chlorine chains are actually broken by oxygen. We must realize that several reactions may take place, for example



or those similar to the postulates of the Haber mechanism¹¹



and, in addition, no one has considered the possible chain breaking abilities of hydrogen peroxide itself:



In conclusion, then, it might be said that, while considerable clarification of our views of the photo combination of hydrogen and chlorine has occurred, there are many aspects of the problem which must be solved before anything like a complete picture can be obtained.

¹ Rodebush and Klingelhoefer, these PROCEEDINGS, 18, 531 (1932).

² Kimball and Eyring, *J. A. C. S.*, 54, 3883 (1932).

³ Bodenstein, *Trans. Faraday Soc.*, 27, 413 (1932).

⁴ Thon, *Z. Physik. Chem.*, 127, 327 (1926).

⁵ Bodenstein and Unger, *Z. Physik. Chem.*, B11, 253 (1931).

⁶ Cremer, *Z. Physik. Chem.*, 128, 285 (1927).

⁷ Ritchie and Norrish, *Nature*, 129, 243 (1932).

⁸ Lavin and Bates, *J. A. C. S.*, 55, 81 (1933).

⁹ Salley and Bates, *J. A. C. S.*, 55, 110 (1933).

¹⁰ Frankenburger and Klinkhart, *Trans. Faraday Soc.*, 27, 431 (1931).

¹¹ Professor Bodenstein in a private communication has informed the author that the result of a study of these reactions is being published from his laboratory.

REVERSIBLE COAGULATION IN LIVING TISSUE. XI*

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It has been pointed out, in several of the reports¹ that have been made during the progress of the investigation of reversible agglomeration in living tissue, that sodium rhodanate antagonizes alcohol physiologically. This fact has been utilized successfully in the experimental treatment of seven cases of chronic alcoholism. Much the same theoretical and practical considerations apply here as in the treatment of morphinism. Therefore, other than to point out that at the present time it is impossible to cure the chronic alcoholic who indulges merely because of the euphoria that is produced, it is not necessary to go into the theoretical details. Sodium rhodanate will help to prevent a return to the use of alcohol by