THE JOURNAL

OF THE

American Chemical Society

with which has been incorporated the

American Chemical Journal

(Founded by Ira Remsen)

THE "ACTIVATION" OF CHLORINE

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The large number of papers on the nature of the photochemical re-
action between chlorine and hydrogen is evidence of the fundamental
significance of this still unsolved problem.   That a reaction takes place,
especially under the influence of the shorter wave lengths, and that it
is the chlorine which is effective in absorbing the radiant energy is es-
tablished, but almost every concomitant fact has been repeatedly as-
serted and denied by various investigators.   The recent discovery of
the ozone form of hydrogen,[1] however, suggests strongly that chlorine
also may exist in some similar active modification, and calls for a re-
examination of the evidence.   The work here reported shows that if such
an active form exists at all, it returns to the ordinary form within a very
small fraction of a second, but that, nevertheless, an increased activity
can be imparted to the chlorine by previous exposure to light such that
the period of induction of the photochemical reaction with hydrogen is
reduced or eliminated, this condition lasting for hours or days, but not
indefinitely.

William Cruickshank, who first studied this photochemical reaction,
observed[2] that the reaction is first hesitant, and requires several minutes
before it attains a constant maximum velocity.   This "period of induc-

¹ THIS JOURNAL, 42, 928 (1920); 44, 510 (1922).
² Cruickshank, Nicholson's J., (i) 5, 202 (1801).

tion" has been confirmed by Dalton,[3] Draper,[4] Bunsen and Roscoe,[5] Pringsheim,[6] Bevan,[7] Mellor[8] and Chapman.[9]   What is of interest from our present point of view is the possibility that the reaction of the chlorine with hydrogen is a secondary consequence of the action of the incident light, and that the primary action, occurring during the period of induction, is an activation of the chlorine.

Draper has asserted that chlorine can be activated.   He prepared 2 like samples of the gas, and after keeping one in the dark, but exposing the other to light, he mixed both samples with hydrogen, and showed that the one which had been insolated reacted with the hydrogen at once, while the other required an appreciable period of induction; Bunsen and Roscoe were unable to confirm this experiment; but 50 years later Bevan achieved results similar to those of Draper.   Since then Mellor has denied the possibility of such an activation, chiefly on the basis of thermochemical data, including the work of Favre and Silbermann.[10] We have now repeated Draper's experiment, and confirm his observation.

Destruction of the Latent Period.—The experiments which confirm the effect noted by Draper and by Bevan were as follows.   A 1cm. glass tube, uniform in bore, was cut into two 40cm. lengths, each piece being provided with a paper scale.   At the upper end of each was sealed a 2-way stopcock for evacuating and filling.   The lower end dipped into a beaker containing saturated sodium chloride solution in which chlorine gas is practically insoluble while hydrogen chloride is readily soluble. In a very dim red light both tubes were filled to exactly half their volume with purified chlorine.   While one tube was kept in the dark the other was then exposed to bright direct sunlight for 15 minutes.   Pure hydrogen from a Kipp generator, dried by passage through several towers of sulfuric acid, was then introduced, the volume being exactly equal to that of the chlorine.   The tubes were then exposed side by side to the light from two 100-watt nitrogen-filled tungsten lamps placed at a distance of 25 cm. The linear rise of the salt solution as the hydrogen chloride was formed

[3] Dalton, "A New System of Chemical Philosophy," I.   London, **1809**, p. 300.

[4] Draper, "Scientific Memoirs."   Harper, New York, **1878**, pp. 245–315.   Also *Phil. Mag.*, [3] **23**, 491 (1843); **25**, 9 (1844); **26**, 473 (1845); **27**, 327 (1845).

[5] Bunsen and Roscoe, *Pogg. Ann.*, **96**, 373 (1855); **100**, 43, 481 (1857); **101**, 235 (1857); **108**, 193 (1859); **117**, 529 (1862).   *Phil. Trans. Royal Soc.*, **146**, 355, 381, 601 (1857); **148**, 879 (1859).   Ostwald's "Klassiker der Exacten Wissenschaften," Nos. 34 and 38.

[6] Pringsheim, *Wied. Ann.*, **32**, 384 (1887).

[7] Bevan, *Proc. Roy. Soc.*, **72**, 5 (1903).   *Proc. Cambridge Phil. Soc.*, **11**, 262 (1902). *Phil. Trans. Roy. Soc.*, **202A**, 71 (1904).

[8] Mellor, *J. Chem. Soc.*, **79**, 216 (1901); **81**, 414, 1272, 1280, 1292 (1902).   *Proc. Chem. Soc.*, **53**, 53, 140, 196 (1904).

[9] Chapman, *J. Chem. Soc.*, **89**, 1399 (1906); **95**, 135, 959, 1717 (1909); **97**, 845 (1910); **103**, 496 (1913).

[10] Favre and Silbermann, *Ann. chim. phys.*, [3] **37**, 499 (1853).

and dissolved, was then read on the scale. The tube which was chosen for insolation was alternated in the various runs. In no case was there any notable period of induction in the case of the insolated tube, while the uninsolated tube required 2 minutes of "induction." The average readings from 13 tests given by the insolated sample after 2, 4 and 6 minutes were 2.22, 5.17 and 8.08, respectively. The uninsolated sample gave 0.15, 0.90 and 2.20, respectively.

These figures show that the chlorine undergoes some change in sunlight which enables it to react at once with hydrogen when the mixture is illumined. The change is persistent but not permanent. There was no diminution in the effect when 3 hours were allowed to elapse between the insolation of the chlorine and the addition of the hydrogen. When 24 hours were allowed to elapse, however, the average rise of the insolated sample amounted to only 0.40 during the first 2 minutes, while that of the uninsolated tubes was 0.04. When several days had elapsed, both tubes behaved as if uninsolated.

The same effect was noted when a powerful quartz mercury vapor lamp, described in the succeeding section, was used instead of sunlight for the insolation of the chlorine. The intensity of the actinic ultraviolet light from this lamp was at least a hundred times that of sunlight.

The Attempts to Activate Chlorine.—A possible explanation of this apparent activation is that the chlorine undergoes some molecular transformation into an active form. The fact that the apparent activation persists for many hours is evidence that the active form is not that of single atoms; they would recombine into the ordinary molecular form in a brief time. For the same reason free electrons or ions cannot be responsible. Since hydrogen, however, can exist in the form of tri-atomic molecules, chlorine may also. The ozone form of hydrogen reverts to the ordinary form within a minute or two, but such a form of chlorine might be more stable. The test that presents itself consists in the illumination of the chlorine and its subsequent reaction with hydrogen *in the dark*.

In all the work heretofore mentioned, the mixture of gases has been exposed to light to produce the reaction. Several attempts have, however, been made to cause the reaction to take place in the dark after insolation of the chlorine alone. Successful attempts are reported by Von Cordier[11] and Kellner[12] and Russ;[13] but the attempts of Askenasy and Meyer,[14] Vernon,[15] Shenstone,[16] and Foster[17] were failures.

[11] Von Cordier, *Monatsh.*, **21**, 184 (1900).

[12] Kellner, *Z. Elektrochem.*, **8**, 500 (1902).

[13] Russ, *Ber.*, **38**, 1310 (1905).

[14] Askenasy and Meyer, *Ann.*, **269**, 72 (1892).

[15] Vernon, *Chem. News*, **63**, 67 (1891).

[16] Shenstone, *J. Chem. Soc.*, **71**, 486 (1897).

[17] Foster, *Ber.*, **38**, 1781 (1905).

Much of this work is qualitative, yet a careful study by Bodenstein[18] in the course of his investigation with Dux[19] and with Taylor[20] of the kinetics of the chlorine-hydrogen reaction established that a 25 candle-power tungsten lamp at 30 cm. distance does not activate chlorine sufficiently to enable it to react with hydrogen in the dark, even when the two gases are mixed in the dark within 0.00065 seconds from the time of exposure of the chlorine.

There remains the possibility that more powerful illumination would produce activation. We, therefore, undertook the study with the aid of a powerful quartz mercury lamp of the type described by Bovie,[21] which will carry 15 amperes at 220 volts, or more than 3,000 watts, giving an arc 60 cm. in length, of more than 1,000 candle-power, and extremely rich in ultra-violet rays which are strongly absorbed by chlorine and hence effective in producing the photochemical reaction. Such a lamp was placed at our disposal by the Committee on Grants for Research of the American Association for the Advancement of Science, to whom we cordially express our gratitude. While some minor modifications were made in our design of the lamp, the diagram given by Bovie will suffice, and the letter references given are to his drawing.

Chlorine was obtained from a commercial tank. It was freed from hydrochloric acid by slow passage through a long tube containing granulated manganese dioxide kept at 100° by means of a surrounding tubular jacket through which steam circulated. That hydrogen was not present, and that hydrogen chloride was completely removed were shown by the absence of any test for chloride in the preliminary tests. The chlorine was dried by bubbling through 2 Emmerling towers containing glass beads and sulfuric acid, and by passing through a long tube containing phosphorus pentoxide. Hydrogen was also obtained from a commercial tank and freed from oxygen by passage through a silica tube containing platinized asbestos kept at red heat by external electric heating. It was dried both before and after this treatment by passage over lumps of fused potassium hydroxide in 2 sets of 2 Emmerling towers, and finally by passage over phosphorus pentoxide.

The chlorine entered the illuminating chamber at V, passing through the tubular jacket, S, which surrounds the mercury arc in the central quartz tube of the lamp. It passed on through the capillary outlet at U and immediately entered a 3-way capillary stopcock. This cock and all glass parts beyond it were heavily painted with black asphalt paint to exclude daylight. Hydrogen entered through the side branch of the 3-way stopcock, and mixture took place within the capillary of the stopcock. No provision was made to prevent the diffusion of the hydrogen back against the chlorine stream into the lamp, with the exception that the chlorine stream was passed at a rate of about 135 cm. per second through the capillary whenever hydrogen was admitted. That this was effective is shown by the fact that no runs gave evidence of the formation of hydrogen chloride. The hydrogen was admitted into the stopcock, however, through a shallow mercury

[18] Bodenstein, Z. Elektrochem., 22, 202 (1916).

[19] Bodenstein and Dux, Z. physik. Chem., 85, 297, 329 (1913).

[20] Bodenstein and Taylor, Z. Elektrochem., 22, 54 (1916). Taylor, THIS JOURNAL, 37, 24 (1915).

[21] Bovie, THIS JOURNAL, 37, 1721 (1915).

trap to prevent the back diffusion of the chlorine into the hydrogen purifying system. Before this was done, occasional deceptive tests for hydrogen chloride were obtained, but with the trap in operation it was always possible to obtain the mixed gases free from any accidental contamination with hydrogen chloride. This was proved by many negative tests.

To determine the small amount of hydrogen chloride in the presence of a preponderance of chlorine, the mixed gases were passed into a blackened Meyer absorption bulb containing 10% neutral potassium iodide solution. Iodine was precipitated by solution of the chlorine, and the hydrogen chloride went into solution as hydrochloric acid. That solution of the hydrogen chloride was effected, was shown by the appearance on analysis of traces of acid when, in the preliminary experiments, chlorine was allowed to diffuse back into the hydrogen tubes exposed to weak diffused daylight. When potassium iodide is used in sufficient excess, the solution of the chlorine generates no permanent acidity, as was shown by our large number of negative tests for acid. The solution was washed from the absorption bulb system into a beaker, and titrated with 10% sodium thiosulfate solution to determine approximately the amount of chlorine dissolved, and to bleach the iodine color; and was thereafter titrated with 0.01 N sodium hydroxide solution to determine acidity. Methyl red was used as indicator in this titration, as it changes at a hydrogen-ion concentration of 10^{-6}. When a trace of hydrogen chloride was known to be present, as much as 1 cc. of alkali was required, but when all extraneous sources of hydrogen chloride had been eliminated, the solution itself, before the addition of alkali, showed the yellow alkaline color of methyl red, thus showing the absence of all acid.

In no case was there any evidence of the formation of hydrogen chloride. Several dozen tests were made, extending up to half an hour's passage of a steady and rapid chlorine stream. In several tests a rapid stream of cold water was allowed to run directly over the quartz lamp tube, between it and the quartz jacket through which the chlorine was passing, thus eliminating any effect from the heat of the lamp. In others, a concentrated solution of ammoniacal cupric sulfate was placed in the tubular space between the lamp and the quartz jacket in order to extinguish both the heat rays and the ultra-violet rays, and to secure illumination only by blue light. This was on the supposition that the rays at either end or both ends of the spectrum might be as effective in destroying the desired active modification of chlorine as in forming it. Finally, a closed volume of chlorine was illuminated intensely for 10 minutes and then passed rapidly into the Meyer bulb, mixed with hydrogen on the way.

In no case was any acid formed. Hence the ozone form of chlorine will not explain the photochemical reaction of hydrogen with chlorine unless it be assumed to have a very brief life, certainly less than a second, and probably less than 0.01 second, which was the time interval between illumination and mixture with hydrogen in the above experiments.

There remained the possibility that the ozone form of chlorine can be produced by the electrical discharge, though not by ultra-violet light. This was now excluded by using the same experimental arrangement except for the substitution of a discharge tube in place of the lamp. Two types of discharge were used. One was the brush discharge in a small

glass Siemens ozonizer tube, furnished by a high voltage induction coil. The other was an arc from a 20,000-volt Thordarson wireless transformer passing through chlorine at a pressure of 6 cm. of mercury. Since metallic electrodes are attacked by chlorine, glass-covered mercury electrodes were used in this work. Two 5mm. glass tubes were sealed into the ends of a 20mm. glass tube in such a way as to project into it and leave a gap between them for the arc about 8 cm. in length. The inner ends of the tubes were sealed smoothly round, and the tubes were then filled with mercury, thus forming glass-covered mercury electrodes projecting into the tube. In no case was any acid formed.

There being no evidence for the existence of an active form of chlorine, the explanation of Draper's experiment will be found in that of the induction period itself. The absence of the active chlorine, therefore, makes more attractive recent experiments[9] on the possibility that the latent period is caused by an inhibition, the removal of which is the first action of the light.

Summary

Neither a 3000-watt Bovie mercury arc lamp nor a high potential electric discharge was found to be capable of imparting to chlorine an activity such that it will react with hydrogen in the dark. Draper's experiment, however, was confirmed. The fact that the latent period in the hydrogen-chlorine reaction can be destroyed by previous insolation of the chlorine must be attributed to the destruction of inhibiting impurities rather than to any activation of the chlorine itself.

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THE ELECTROMETRIC STANDARDIZING OF TITANOUS SOLUTIONS. (Preliminary Report)

By W. S. HENDRIXSON AND L. M. VERBECK

The great value of titanous salts in analytical chemistry has become well known through the work of many chemists. Titanous chloride has been used not only in determining inorganic but also many organic substances, which are likely to be colored or to give colored solutions on reduction, thus interfering in the accurate determination of end-points in the usual methods of analysis where colored indicators are used. Such difficulties would, of course, be removed by the application of the voltage method. Moreover, so intensely reducing is the titanous ion that an interval of nearly one volt is given between a slight excess of titanous ion and excess of such oxidizing agents as dichromate and permanganate, when the calomel-platinum cell is used, and this wide interval permits the deter-