

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Atomic Chlorine and its Reaction with Hydrogen¹

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One of the most promising methods of studying the mechanism of gaseous reactions is the introduction of the various atomic species into the reaction mixture. The classical example of such a study is the work of Bonhoeffer on atomic hydrogen.² The most satisfactory method for the production of gaseous atoms is by the high frequency electrodeless discharge. If it is desired to pass the atoms into a reaction chamber, a too high frequency is disadvantageous because the discharge will travel along the tube and affect the reaction. The catalytic effects of walls, water, metals, etc., have been clearly demonstrated in the case of hydrogen atoms but it has been proved in this Laboratory that each species of atom is a law unto itself so far as these effects are concerned.

The Production of Chlorine Atoms.—The thermal and photochemical dissociations of the chlorine molecule have been demonstrated by a number of observers but no one has produced any considerable amount of atoms by this method. The first attempt to produce chlorine atoms in this Laboratory was made with a discharge between cooled copper electrodes in a long tube of the Wood type. The electrodes were not attacked and the discharge could be maintained over a considerable range of pressure but the gas was not dissociated. This type of apparatus was discarded in favor of the electrodeless discharge.

Experimental

Dissociation of Chlorine.—The apparatus is shown in Fig. 1. It consisted of a supply of chlorine, A, a bulb for the electrodeless discharge, E, a diffusion gage, H, liquid air trap, mercury vapor pump and oil pump. The chlorine, prepared from concentrated hydrochloric acid and potassium permanganate, was washed with water, dried by sulfuric acid and liquefied in a bulb of about 30 cc. capacity by a mixture of dry ice and acetone. Moisture was kept out of the vent tube by means of a U-tube kept in the cold bath. The chlorine bulb was connected to the apparatus through a capillary which controlled the flow. The bulb was held at a temperature of -80° .

The discharge was produced in a 200-cc. Pyrex bulb. The energizing circuit was connected as shown. A 2.5 k. v. a., 25,000 volt Thordarson transformer was used. The condenser D consisted of 14 plates, about 20 by 23 cm., separated by about 5 mm. of window glass, the whole being immersed in insulating oil. The spark gap, F, of about 1 cm. width, had zinc electrodes about 3 cm. in diameter. The gap was mounted in a sound-proof box fitted with an air connection for cooling the electrodes and regulating the voltage drop. The coil, which was fitted closely to the bulb, was made in two parts of five turns each. It was carefully grounded near the center in order to reduce the stray discharge into the remainder of the apparatus. When this was properly done no discharge could be seen in a dark room at more than about 5 cm. distance from the bulb.

(1) A preliminary notice of this work has been published in the *Proceedings of the National Academy of Sciences*, **18**, 531 (1932).

(2) Bonhoeffer, *Z. physik. Chem.*, **113**, 199 (1924).

All of the connections in the high frequency circuit were made with 3-mm. copper tubing. The current in the primary of the transformer was usually about 15 amperes and was regulated by a series resistance, B, and the air flow at the spark gap to give the best glow discharge.

The diffusion gage H was used to detect the atoms produced. It was similar to the gage described by Wrede.³ It consisted of an orifice 0.1 mm. in diameter and gages for measuring the total and differential pressures. The orifice was made in a thin glass film sealed on the end of a 5-mm. tube which extended into the gas stream at a point about 7 cm. from the discharge bulb.

The film was made by blowing out a glass bubble until it was thin enough to show colors. It was sealed to the tube by heating the latter and sticking it into the glass bubble. The hole in the film was controlled by the energy of the spark. The size of the hole was controlled by the energy of the spark. The gages were of 5-mm. tubing and were filled with a heavy paraffin oil which was found to be unaffected by the chlorine. Gage J measured the total pressure; I, the pressure difference across the orifice. A cathetometer sensitive to 0.01 mm. was used to read the oil levels. The gage was compared to a McLeod gage using hydrogen in a static system. A 1-mm. differential on the oil gage corresponded to 0.06 mm. of mercury. Thus a pressure difference of 0.0006 mm. of mercury could be detected. The diffusion gage required about two minutes to come to equilibrium after small pressure changes.

The gages were kept in a bath of oil to reduce temperature variations. Oil vapors were kept out of the rest of the apparatus by means of the traps T_1 and T_2 which were kept in a carbon dioxide-acetone mixture. At first the orifice chamber was cooled by an air blast, later it was placed in a thermostat.

The glow discharge was obtained from very low pressures up to about 1 mm. At the lower pressures the glow spread throughout the bulb and was of a bright greenish-blue color. The discharge would not start itself at a pressure above about 0.6 mm., but once started, it continued to operate until an upper limit was reached at about 1 mm. At the higher pressures the discharge took on a ring form.

The degree of dissociation measured by the diffusion gage increased with the chlorine flow. In the range of 5 to 10 cc. per minute generally used here this change was small. With chlorine pressures between 0.2 and 0.7 mm., the degree of dissociation varied between about 0.08 and 0.18, tending to decrease at the higher pressures. When the temperature of the orifice chamber and leads was varied from -80 to 100° the dissociation increased from 0.04 to 0.09. This change was probably due to the more rapid motion of the gas at the higher temperature.

After a few hours of operation the discharge bulb became coated with a white

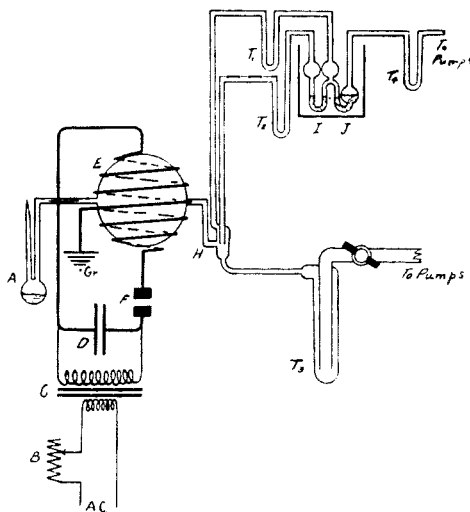


Fig. 1.

(3) Wrede. *Z. Physik*, **54**, 51 (1929).

deposit. After a longer time the connecting tubes showed a similar deposit. When the bulb was cooled by a blast of air less of this material formed. It was found to sublime slowly when heated to redness in air. It was insoluble in water and the common acids. The degree of dissociation did not change greatly with time, showing that the deposit had little activity for the recombination of chlorine atoms.

Properties of Atomic Chlorine.—To obtain some information concerning the catalytic activity of materials for the combination of the atoms, the method which Bonhoeffer² used with atomic hydrogen was chosen. The method consists of coating the materials on the bulb of a thermometer placed in the active gas and observing the temperature rise. The apparatus was similar to that used above, except that the Wrede gage was replaced by a tube to contain the thermometer. The bulb of the thermometer was directly in the gas stream about 7 cm. from the discharge bulb. The materials were either placed directly on the bulb or on a thin glass cap which fitted closely over it. The apparatus was cooled by an air blast. The results are shown in Table I.

TABLE I
CATALYTIC ACTIVITY IN CHLORINE RECOMBINATION

Material	Maximum temperature, °C.	Material	Maximum temperature, °C
Pyrex glass	30	NaCl, fused	34
Ag foil	115+	KCl, fused	70
Cu foil	115+	AgCl, fused	91
Al foil	82	CaCl ₂ , fused	66
Ni wire	120	CoCl ₂ , evap.	72
Platinized glass	35	Gas carbon	115+

The silver and copper were rapidly attacked, forming an adherent layer of chloride. The aluminum and nickel showed no sign of attack. Sodium chloride, potassium chloride and platinum were erratic in behavior, some samples heated rapidly, others not at all. Their activity was always lost after running for some time.

The pressure difference produced at the diffusion gage and the heating effect produced with some materials showed conclusively that we produced chlorine atoms and not more complex molecules. Since chlorine attacks silica at high temperatures to produce silicon tetrachloride it is not surprising that the atoms attack glass at moderate temperatures. The products would of course be different. The deposit observed could not have been one of the normal chlorides of silicon or boron since these are quite volatile.

The fact that the atoms can pass through a tube at a temperature much below the normal boiling point for the liquid is very unusual. Hydrogen, oxygen and nitrogen atoms are all condensed when passed into a liquid air trap. This difference in behavior may be due to the fact that these latter gases need a certain water content to prevent recombination while chlorine

does not. If water had been required with chlorine the study of its reaction with hydrogen would have been made difficult if not impossible.

The data obtained with catalysts for the recombination showed which materials should be avoided in order to reduce recombination, and which may be used to aid recombination. Thus silver was chosen for use in the diffusion gage and for stopping the reaction. Silver, copper, nickel, carbon and similar materials were carefully excluded from the rest of the apparatus.

The recombination on glass, sodium chloride, potassium chloride and platinum was small, but the method was not sensitive enough to distinguish between them in activity. The initial activity observed with platinum, sodium chloride and potassium chloride may have been due to impurities which later volatilized. The low activity of platinum and sodium chloride agrees with the results of Senftleben and Polanyi.⁴

Silver should be a good material for detecting chlorine atoms in a molecular ray or elsewhere. Their action on a thin mirror surface was particularly noticeable. The mirror remained bright on the glass side for several days when exposed to dry chlorine, but immediately turned white and translucent when treated with atomic chlorine.

In view of the great catalytic activity of copper it seems remarkable that Jost and Sweitzer⁵ were able to pass activated chlorine through a copper capillary while Bodenstein and Taylor⁶ and others were unable to pass it through glass capillaries at somewhat smaller velocities.

The Reaction of Chlorine Atoms with Hydrogen.—The apparatus used is shown in Fig. 2. It consisted of a chlorine supply, A, a hydrogen leak, F, the discharge bulb, B, Wrede gage, C, with oil manometers G and H, reaction tube, D, and the sampling train of liquid air traps T₆ to T₁₁. Traps T₆, T₇ and T₁₂ were made with ground joints.

The chlorine bulb was kept in a large Dewar half filled with ethyl acetate at its melting point. A metal tube was provided for cooling with liquid air. The mixture was thoroughly agitated by a screw stirrer. A toluene thermometer was used to observe the temperature, which could be kept between -83.5 and -84.0° . Mixtures of carbon dioxide with alcohol or acetone were found unsatisfactory as they became several degrees cooler when chlorine was used, due to the heat absorbed by vaporization.

The hydrogen was taken from a commercial cylinder. It was bubbled through water into a gas buret which was used to measure the rate of flow. The flow was regulated by the capillary leak, F. Moisture was removed by trap T¹ which was immersed in liquid air.

The discharge bulb and coil circuit were of the same type as described above. The arrangement of the reaction tube and diffusion gage was changed with the different experiments and will be described later. They

(4) Senftleben, *Z. Physik*, **32**, 922 (1925); Polanyi and Bogdandy, *Z. Electrochem.*, **33**, 554 (1927).

(5) Jost and Sweitzer, *Z. physik. Chem.*, **13B**, 373 (1931).

(6) Bodenstein and Taylor, *Z. Electrochem.*, **22**, 202 (1916).

were placed in a small thermostat which was controlled to 0.1° . A catalyst of silver foil was used in the gage for the recombination of chlorine atoms.

The connection used to lead the chlorine into the reaction tube was adjusted to the chlorine flow to prevent the diffusion of hydrogen back into it. When the total pressure was about 0.4 mm. and the tube was small enough to cause a pressure drop of about 0.1 mm. between the discharge bulb and the reaction tube no diffusion took place. This was shown by the fact that the spectrum of the discharge was not changed when the hydrogen flow was started. The degree of dissociation also remained the same. Since the discharge could not be maintained at a pressure much above 1 mm. and the diffusion gage required a pressure of 0.5 mm. or less, the method was applicable only within the pressure range of 0.3 to 0.5 mm.

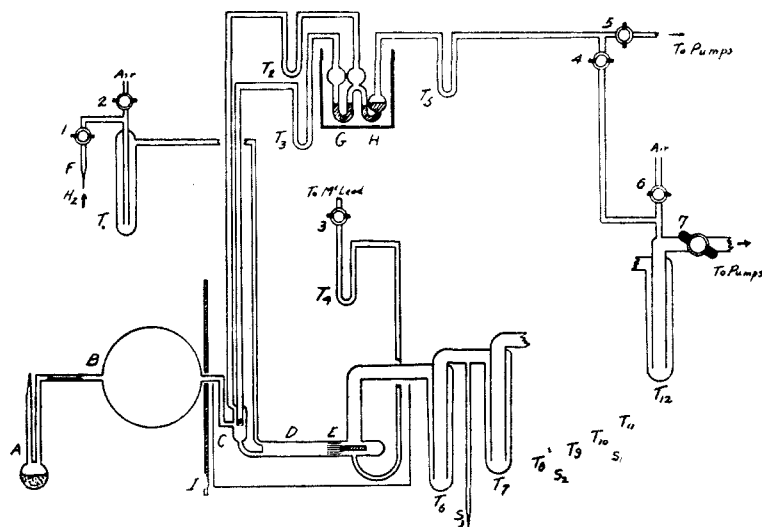


Fig. 2.

No sealing wax was used in the construction of the apparatus and the reaction mixture was protected from stopcock grease by liquid air traps.

Samples of the products were taken by placing Dewar flasks of liquid air on the sampling traps. The time of sampling, which was usually five or ten minutes, was terminated by placing liquid air on the next trap to the left. Conditions could then be changed and another sample taken.

When all the samples were taken, the discharge was turned off, and the pumps and hydrogen shut off. The samples were swept out one at a time through the sampling tubes after removing the liquid air from the corresponding traps. The chlorine and hydrogen chloride were absorbed in 200 cc. of 5% potassium iodide solution. Several tests showed that this procedure removed all of the chlorine and hydrogen chloride from the trap. The air flowing from both sides prevented the diffusion of the chlorine or

hydrogen chloride into the other traps which were still cooled with liquid air.

The samples were analyzed by titrating with 0.20 *N* sodium thiosulfate without an indicator, then with 0.10 *N* potassium hydroxide using methyl orange indicator. All of the solutions were made from conductivity water which was also used in rinsing. Numerous blank runs were made to check the neutrality of the solutions and of the chlorine.

Extent of Reaction.—A reaction bulb of about 35 cc. volume was used. The diffusion gage was sealed directly into one side of the reaction bulb. It was connected to the discharge bulb by 7 cm. of 4 mm. tubing bent twice at right angles. The dissociation was measured at the beginning of each run before the hydrogen flow was started. The reaction was probably not confined to the reaction bulb, but also took place in the connecting tubes to the sampling traps which were at room temperature. The results are shown in Table II, the temperature given is that of the thermostat. The pressure was 0.4 mm. and the hydrogen flow 17.5 cc. per minute.

TABLE II

EXTENT OF REACTION WITH HYDROGEN			
Temp., °C.	Cl ₂ , cc./min.	Dissociation	Cl ₂ reacting, %
0	7.0	0.20	52
36	10.4	.20	97
99	8.8	.20	96
0	7.5	.07	24
25	7.9	.07	83
50	8.4	.07	99

It was observed that when the reaction bulb was not placed in the thermostat it became hot. The reaction then ran nearly to completion even with a very low degree of dissociation.

When there was an excess of chlorine, the hydrogen was sometimes completely used up, as shown by the very slow pressure increase when the pumps were shut off. The results were the same when the room was darkened to prevent the occurrence of a photochemical reaction. Blank tests with hydrogen and chlorine, but with the discharge off, showed no hydrogen chloride formation in either a darkened or a light room.

No reaction was observed when the current was not great enough to form a glow in the discharge bulb. With this arrangement a weak static discharge took place in the connecting tubes, but no dissociation could be detected by the gage.

Effect of Oxygen.—The same apparatus was used except that a bulb which had been silvered inside was placed after the reaction bulb. That it stopped the reaction beyond this point was shown by the fact that the silver was attacked only at the inlet. The hydrogen flow was 6.7 cc. per minute and a flow of 0.08 cc. per minute of oxygen was added to it by means of a

capillary leak. The chlorine flow was about 9 cc. per minute. Its dissociation was measured before and after each run; the average was about 0.04. Samples were taken with the oxygen flow on and then with it turned off.

The average yields, expressed as percentage of the chlorine reacting, were: with oxygen 21% at 0° and 38% at 25°; without oxygen 25% at 0° and 36% at 25°.

Effect of Surface.—The effect of surface was studied using an empty Pyrex bulb of about 60 cc. volume, and the same bulb filled with short lengths of 4-mm. Pyrex tubing. The surface to volume ratio was changed from 2 to 10. The apparatus was thoroughly cleaned with hot $\text{CrO}_3 \cdot \text{H}_2\text{SO}_4$. The diffusion gage was arranged as in Fig. 2 and the chlorine was mixed with the hydrogen just at the inlet to the bulb. The dissociation was measured for each sample and was about 0.10.

The yields, calculated as the molecules of hydrogen chloride formed per chlorine atom introduced, were 3.1 and 5.0 at 0 and 25° for the packed bulb, and 2.8 and 3.8 at 0 and 25° for the empty bulb.

Rate of Reaction.—The apparatus is shown in Fig. 2. The light of the discharge was screened off by the shield I. The connecting tube from B to C was a 6 cm. length of 6 mm. tubing, that from C to D was a 1.5 cm. length of 4 mm. tubing. The reaction tube D was about 1.3 cm. wide and 8 cm. long and was calibrated from the inlet side. The system was made quite small in order to keep the amount of reaction small and the partial pressures of chlorine atoms and hydrogen nearly constant.

The reaction was stopped at the desired time by a roll of silver foil about 1 cm. wide shown at E. It caused all the atoms to recombine. A glass covered iron armature fastened to the silver foil made it possible to move it by means of a magnet and hence to vary the time of reaction.

The pressure of the reacting mixture was measured by a McLeod gage with a ratio of 875 to 1. The dissociation was measured twice for each sample and the readings were averaged. The time required for the chlorine to pass from the discharge bulb to the reaction tube was about 0.015 second.

Results.—When the silver foil was placed about 2 mm. from the inlet end of the reaction tube, the amount of reaction was very small. This showed that the foil was very effective in stopping the reaction and that no hydrogen was diffusing into the chlorine leads.

The data for a typical run are given below

Reaction volume.....	10 cc.
Hydrogen flow.....	6.3 cc. per minute
Pressure.....	0.340 mm. of mercury
Time of sampling.....	10 minutes
Reaction temperature.....	0.0°
Temperature of chlorine.....	-83.5°
Total pressure at diffusion gage.....	7.00 mm. of oil

Differential pressure across orifice.....	0.40 mm. of oil
Degree of dissociation of chlorine.....	0.11
Thiosulfate titration.....	36.5 cc. of 0.20 <i>N</i>
Potassium hydroxide titration.....	9.1 cc. per minute
Chlorine flow.....	9.1 cc. per minute
Per cent. of chlorine reacted.....	10.2
Hydrogen chloride formed per Cl atom introduced..	0.92
Time of reaction.....	0.016 seconds
Number of collisions per Cl atom.....	30×10^8
Probability for reaction.....	1.5×10^{-5}

The last two entries were calculated by the kinetic theory. The number of collisions, Z , which a molecule of type I (Cl) makes with molecules of type II (H_2) per second is

$$2N_2 \left(\frac{d_1 + d_2}{2} \right)^2 \sqrt{\frac{m_1 + m_2}{m_1 m_2}} \sqrt{2\pi kT}$$

N_2 is the number of type II molecules in volume V , d_1 and d_2 are the collision diameters, and m_1 and m_2 are the corresponding masses. The diameter of the chlorine atom is not known. The value given for argon ($d = 2.97 \times 10^{-8}$)⁷ was used. The value for hydrogen ($d = 2.39 \times 10^{-8}$) was taken from the same source.

The average number of collisions, Z' , which a chlorine atom experienced while in the reaction tube is

$$Z' = Z n V_R / N_T$$

Where n is the total number of molecules per cc. in the reaction tube of volume V_R , and N_T is the total number of molecules entering the tube per second.

It was assumed that the reactions involved were



and that the rate of (II) was greater than the rate of (I). Thus each chlorine atom which reacted would form 2HCl . The ratio of HCl formed to the Cl introduced was found by dividing the fraction of chlorine which reacted by the degree of dissociation.

The probability, W , of a chlorine atom reacting with a hydrogen molecule on collision is

$$W = (\text{HCl}/\text{Cl})/2Z'$$

The results of the other rate measurements are shown in Table III. The temperature is in degrees centigrade, pressure in mm. of mercury, and reaction volume in cc. The values in the columns headed H_2 and Cl_2 are the corresponding rates of flow in cc. at N. T. P. per minute. The degree of dissociation of the chlorine (α) is given in column 6. Column 8 gives the yield of HCl per chlorine atom calculated from the dissociation

(7) "Treatise on Physical Chemistry," 2d ed., D. Van Nostrand Co., New York, 1931, p. 249.

and the amount of HCl formed. Column 9 gives the number of collisions (Z') one chlorine atom had with hydrogen molecules in passing through the reaction tube. The probability (W) of a chlorine atom reacting with hydrogen on collision is given in column 10.

TABLE III
RATE OF REACTION OF ATOMIC CHLORINE WITH HYDROGEN

Test	T	P	V	H_2	α	Cl_2	HCl/Cl	$Z' \times 10^{-3}$	$W \times 10^5$
1	0.0	.30	9.3	6.6	.049	9.8	0.57	21	1.4
2	.0	.30	9.3	6.6	.042	10.1	.62	21	1.5
3	.0	.30	9.7	6.6	.050	9.2	.62	24	1.3
4	.0	.30	9.7	6.6	.050	9.0	.64	26	1.2
5	.0	.31	9.7	6.3	.050	9.4	.62	25	1.2
6	.0	.29	4.8	6.3	.056	9.6	.23	10	1.2
7	.0	.28	4.8	6.3	.062	10.1	.30	9.2	1.6
8	.0	.30	9.7	6.3	.065	10.0	.58	21	1.4
9	25	.27	9.4	6.4	.110	9.7	.93	14	3.3
10	25	.27	4.8	6.4	.110	9.5	.59	7.6	3.8
11	25	.28	4.8	6.7	.070	9.7	.47	8.5	2.8
12	25	.30	9.7	6.7	.066	9.2	1.05	21	2.5
13	25	.29	9.7	6.6	.090	9.7	0.78	18	2.2
14	25	.28	9.7	6.6	.087	10.2	.75	16	2.3
15	0.0	.32	9.7	6.6	.048	9.7	.40	26	0.8
16	.0	.32	9.7	6.6	.051	9.0	.46	27	.8
17	.0	.34	10	6.3	.110	9.1	.92	30	1.5
18	.0	.33	10	6.3	.110	9.4	.90	27	1.7
19	25	.30	10	6.3	.20	8.2	1.43	21	3.4
20	25	.31	5.0	6.4	.114	9.4	0.55	10	2.8
21	25	.32	5.0	6.4	.106	9.7	.47	11	2.1
22	0.0	.32	5.0	6.4	.077	10.7	.16	11	0.7
23	.0	.31	5.0	6.4	.070	10.7	.15	11	.7

The reaction tube was cleaned after test 12. A new reaction tube, orifice chamber and discharge bulb was placed in the apparatus before test 17.

Following these tests a glass plate was placed before the silver catalyst. The clearance around the edge of the plate was about 0.5 mm. and its presence caused a pressure drop of about 0.2 mm. It should have prevented a lowering of the concentration of atomic chlorine by diffusion to the catalyst. The yield was somewhat higher, but since the pressure was uncertain, the collisions could not be calculated.

A run was also made in which the hydrogen was saturated with water vapor at room temperature. There was slightly less reaction than with the dried gas. A maximum value for the water in the chlorine may be calculated from the vapor pressures. The vapor pressures of chlorine and ice at -80° are 58.7 mm. and 0.0004 mm., respectively. At the operating pressure this would give a partial pressure of water vapor of about 10^{-6} mm. Since the chlorine was dried before being liquefied this figure is probably much too high.

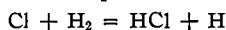
The saturated hydrogen contained about 3% water vapor. This would give a partial pressure of water vapor of about 0.003 mm. in the reaction tube, at least 3000 times that in the dry gases.

Discussion of the Chlorine-Hydrogen Reaction.—The reaction of chlorine with hydrogen has been the subject of so many studies that complete references cannot be given here.⁸ The original mechanism proposed by Nernst is a chain involving two steps



It has been generally accepted that (2) takes place and that it is a rapid reaction. Bodenstein has estimated a reaction probability of 10^{-3} per collision for (2). Most of the discussion has centered around (1). The question concerning this step in the reaction apparently was raised by the work of Coehn and Jung,⁹ who claimed that a trace of water was necessary for the photochemical reaction. It seemed necessary to introduce water into the reaction mechanism somewhere and various proposals were made which involved replacing (1) by various complicated mechanisms.

The experiments reported above prove conclusively that the reaction



does take place, at least at low pressures.

The completeness of the reaction, when allowed to run in a fairly large volume, shows that a chain reaction takes place. The chains are short, due to the large number of chlorine atoms introduced compared to the total reacting mixture. This fact also accounts for the lack of any effect of light on the yields. The number of atoms which could be formed by light absorption under the experimental conditions would be very small compared to the number present.

The negligible effect of additional surface of Pyrex glass was due to its small activity for recombination of chlorine atoms. Since hydrogen atoms recombine rapidly on dry glass surfaces, this effect shows that either the hydrogen atoms react very rapidly with chlorine or that their recombination is prevented by a layer of chlorine adsorbed on the glass.

The absence of an appreciable retardation of the reaction by oxygen was due to the shortness of the chains. Photochemical work has shown that the effect of oxygen is very great when the chains are long, but small when the chains are short.

The largest source of error in measuring the rate of reaction was the recombination of the atoms on the walls. A clean glass surface was only slightly active, but the activity increased with the time of operation. This is shown in Table III by tests 9 to 14. The probability of reaction decreased from about 3.5×10^{-5} to about 2.3×10^{-5} . A similar decrease

(8) For recent references see Bodenstein, *Trans. Faraday Soc.*, **27**, 413 (1913); Kassel, "The Kinetics of Homogeneous Gas Reactions," The Chemical Catalog Co., New York, 1932.

(9) Coehn and Jung, *Z. physik. Chem.*, **110**, 705 (1924).

is shown by tests 17 to 23. When the reaction tube was kept at 0° all the time the discharge was on, this change was slow. This indicates that some of the material which sublimed from the discharge bulb may have deposited on the walls and increased the atom recombination.

At the lower temperature less of this material could have reached the reaction bulb because of better condensation in the lead tubes.

Another possibility of error was the diffusion of the atoms to the silver catalyst. This would lower the concentration of chlorine atoms in the reacting mixture and make the probability of reaction too low. The experiment with the glass plate for preventing diffusion showed that this effect was not very large. Tests 5 to 12 show that the amount of reaction was nearly proportional to the reaction volume. If the diffusion had been rapid, the amount of reaction should have increased more rapidly than the reaction.

The error in determining the degree of dissociation was about 5%. The rates of flow were known to about 2%. Titration errors of 5% are probable in the amount of hydrogen chloride formed. The total error for all measurements was about 10%.

Allowing for the decrease of reaction with time, the most reasonable values for the probability of reaction on collision are 1.4×10^{-5} at 0° and 3.3×10^{-5} at 25°. The reaction was carried out under conditions in which practically the only moisture present was that coming from the glass, thus approaching the conditions of dryness obtained in the experiments of Coehn and Jung.⁹ The fact that no difference in the reaction was observed when moisture was present throws grave doubt upon their results and makes it unnecessary to speculate upon a mechanism involving the water molecule. This is in agreement with recent work by Bodenstein,¹⁰ who has been unable to confirm the previous work upon the necessity of moisture to the reaction.

Reaction Probability Calculated from the Results of Other Workers.—The photochemical rate of reaction experiment as ordinarily carried out at high pressures with constant illumination upon mixtures of hydrogen and chlorine is a measurement of average chain length only. Since the chain involves at least two alternating mechanisms and the average chain length depends upon the competition of these mechanisms with others, such measurements do not give direct information of reaction probability, heat of activation or any other fundamental property of the reaction. By making a sufficient number of assumptions, however, a figure may be arrived at and calculations have been made by several. The figures obtained vary from 10^{-8} to 10^{-6} for the mechanism (I). The value arrived at by Bodenstein¹⁰ 10^{-4} is in approximate agreement with our result.

It must not be forgotten that in our calculation we assumed mechanism

(10) Private communication.

(II) to be rapid so that two molecules of hydrogen chloride will be formed for each atom of chlorine. If this assumption were not true, the order of magnitude of the reaction probability would be unchanged.

The Heat of Activation of the Reaction.— $\text{Cl} + \text{H}_2 = \text{HCl} + \text{H}$ (I). It was assumed formerly that an exothermic reaction of the type of (I) required no heat of activation. This assumption is certainly not correct. The above reaction is probably exothermic but so long as the heat of reaction is less than the heat of activation it is not of great importance what the sign of the former is. We shall assume that reaction may take place only when the relative velocity in collision exceeds a certain critical value. This is equivalent to assuming that the activation energy is entirely in the form of kinetic energy of translation. Even when the critical energy is exceeded it is not likely that a collision will always result in reaction. Hence we introduce a "steric" factor. The reaction probability f is therefore given by an expression of the form¹¹

$$f = K \left(\frac{1 + E_0}{RT} \right) e^{-E_0/RT}$$

where K the steric factor is presumably independent of temperature. From the ratio of the reaction probabilities at two temperatures we may calculate the value for the activation energy E_0 . The average values obtained for the reaction probabilities at 0 and 25° give a value for E_0 of 6100 cal. The steric factor corresponding to this activation energy is 0.08, but because of the uncertainty of the experimental results only the order of magnitude may be established. The value of E_0 , on the other hand, would not vary by more than 1000–2000 calories for the different reasonable combinations of individual results at the two temperatures.

It is interesting to compare these results with estimates that have been made by others as to the heat of activation. Rollefson and Lindquist¹² were led by a study of the photochemical reaction of iodine monochloride and hydrogen to postulate that only Cl atoms in the $^2\text{P}_{1/2}$ state react with molecular hydrogen. The $^2\text{P}_{1/2}$ state has an energy of about 2500 calories greater than the normal state. It would therefore be necessary to postulate an additional critical energy of collision of about 3500 calories to bring about reaction. On account of the large number of collisions which a chlorine atom undergoes on the average before it reacts with a hydrogen molecule, it seems probable that statistical equilibrium would be established between the $^2\text{P}_{1/2}$ and $^2\text{P}_{3/2}$ states so that the same results should be obtained regardless of the original state of the chlorine atom. In Rollefson and Lindquist's experiments apparently the chlorine atoms reacted with something else much more readily than with hydrogen. Their postulate

(11) Ref. 7, p. 987. The expression given above assumes the total energy of collision to be available for reaction. This is probably not a proper assumption but the value obtained for the heat of activation would not be greatly different in any case. The question will be discussed by one of the authors elsewhere.

(12) Rollefson and Lindquist, *THIS JOURNAL*, **52**, 2793 (1930).

that only the $^2P_{\frac{1}{2}}$ state reacts with hydrogen is therefore not required by the evidence.

Eyring¹³ has calculated the heat of activation of reaction (I) from wave mechanics and obtains a value for E_0 between 14,000 and 25,000 calories according to the assumptions. The agreement is perhaps as good as is to be anticipated.

The authors wish to express their appreciation to Professor Bodenstein for his courtesy in communicating to them his recent experimental results.

Summary

The technique of preparing chlorine atoms has been developed. The conditions favoring recombination of chlorine atoms are not the same as for hydrogen atoms.

When chlorine atoms are introduced into a hydrogen-chlorine mixture at low pressure a chain reaction is started which will run, under favorable conditions, until one of the gases is used up. Oxygen and water are without effect on this reaction and the simple mechanism proposed by Nernst is adequate to account for it.

The reaction probability for the reaction $\text{Cl} + \text{H}_2 = \text{HCl} + \text{H}$ (I) has been estimated to be 1.4×10^{-5} per collision at 0° and 3.3×10^{-5} at 25° . From the temperature coefficient a heat of activation of 6100 ± 1000 calories is estimated.

(13) Eyring, *THIS JOURNAL*, **53**, 2537 (1931).

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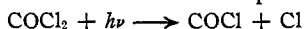
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The Photochemical Oxidation of Phosgene

BY G. K. ROLLEFSON AND C. W. MONTGOMERY

The direct photochemical oxidation of phosgene has never been reported in the literature. It was thought possible that the reaction might take place upon insolation with light of $\lambda < 2700 \text{ \AA.}$, since Henri¹ had found evidence of predissociation of phosgene beginning in this region. The primary act of absorption is believed^{2,3} to lead to the process



in which the intermediate compound COCl is formed. This same intermediate has been postulated in the mechanisms of Bodenstein, Lenher and Wagner⁴ and Lenher and Rollefson⁵ for the photochemical formation of phosgene.

(1) Henri, *Proc. Roy. Soc.*, (London) **A128**, 178 (1930).

(2) Almasy and Wagner-Jauregg, *Naturwissenschaften*, **19**, 270 (1931).

(3) Herzberg, *Ergebnisse exakt. Naturwiss.*, **10**, 207 (1931).

(4) Bodenstein, Lenher and Wagner, *Z. physik. Chem.*, **3B**, 459 (1929).

(5) Lenher and Rollefson, *THIS JOURNAL*, **52**, 500 (1930).