and isothermal compressibility of the following liquids are given: benzene, acetone, ethyl alcohol, methyl alcohol, chlorobenzene, toluene, chloroform, ether, carbon tetrachloride and carbon bisulfide.

The velocity of sound in and the adiabatic compressibility of heptane, octane, aniline, α-bromonaphthalene, glycerin, bromoform and the isomeric heptanes are given.

Some of the compressibility values have been compared with those found by direct measurement by other investigators.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE PHOTOSYNTHESIS OF HYDROCHLORIC ACID AT LOW PRESSURES

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The mechanism of the photochemical combination of hydrogen and chlorine has been the subject of investigation for many years. The results prior to 1926, summarized by Thon,[1] show that the reaction which occurs with the visible and near ultraviolet light must be considered as proceeding according to a chain mechanism starting with the photo-activated chlorine. The nature of this activation has been the subject of speculation, and the assumptions which have been made fall into two groups; first, those that postulate that the light excites the chlorine molecule to a higher quantum state; second, those that consider that the chlorine molecule is dissociated by the light. From the nature of the absorption spectrum of chlorine the dissociation hypothesis is the more probable of the two,[2] and it is the purpose of this paper to present experimental evidence for this view.

Before describing the experimental procedure let us consider what conditions are necessary to show a difference between the two theories. If we have an excited chlorine molecule it may undergo one of the following changes: (1) return to its normal state by emitting light, (2) lose its energy by collision of the second kind, (3) enter into some reaction. At high pressures an excited molecule undergoes so many collisions in its life period that the number returning to the normal state by fluorescence is negligible, but as the pressure is reduced the number fluorescing increases until, at such low pressures that the time between collisions is long compared to the life period of the excited molecule, fluorescence is practically the only process involved. On the other hand, if the chlorine is dissociated

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[1] Thon, *Fortschritte Chem., Physik, physik. Chem.*, **18**, No. 11 (1926).

[2] For this interpretation of the chlorine spectrum see Franck, *Trans. Faraday Soc.*, **21**, 536 (1925); and Kuhn, *Z. Physik*, **39**, 77 (1926).

by light into a normal and an excited atom in the $^2P_1$ state[2] the possibility of fluorescence is eliminated[3] and the life periods of the normal and excited atoms are so long that even at low pressures there remains a great probability that they will enter into reaction. Therefore, if we study the photochemical reaction rate at various pressures, we should find that the velocity constant would decrease rapidly at very low pressures if the active form of the chlorine is an excited molecule, but if the active substance is a normal or an excited chlorine atom the velocity constant should be independent of the pressure.

The pressure at which this difference should appear may be estimated with the aid of the kinetic theory. The number of collisions which a molecule suffers in a mixture of two gases is given[4] by

$$Z_1 = \sqrt{2N_1}\pi\sigma_1{}^2\overline{C}_1 + \sqrt{\frac{m_1 + m_2}{m_2}}\, N_2\pi\sigma_2\overline{C}_1$$

where Z_1 is the total number of collisions per second for a molecule of Type 1, N_1 is the number of molecules of Type 1, N_2 the number of Type 2, $\overline{C}_1$ is the mean velocity of the molecule of Type 1, σ_1 the diameter of the molecule of the first kind and σ_2 the average molecular diameter of the two kinds of molecules. The first term represents the number of collisions of the molecule with other molecules of the same kind, the second term gives the number of collisions with those of the other kind. It readily follows that the time between collisions of a chlorine molecule with a molecule of another kind is given by

$$\frac{1}{\sqrt{\frac{m_1 + m_2}{m_2}}\, N_2\pi\sigma^2\overline{C}_1}$$

The only uncertain quantity in this expression is σ, the molecular diameter, and it is sufficiently accurate for this calculation to assume a value of 3×10^{-8} cm. At a pressure of 0.1 mm. of the other gas the time between collisions is 7.6×10^{-7} sec. According to the work of Wien[5] and Kerschbaum,[6] the life periods of atoms in excited states, which are not metastable, range from 0.1 to 1.5×10^{-7} sec. It seems reasonable to assume that the life period of an excited chlorine molecule is of the same order of magnitude and, therefore, if we are dealing with a reaction between an excited chlorine molecule and some other molecule, we should expect the rate

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[3] The transition from the $^2P_1$ to the $^2P_2$ state of the chlorine atom with emission of light is forbidden by the selection principle for azimuthal quantum numbers. The other possibility, namely, the recombination of the normal and excited atoms with the emission of light can be neglected since the extremely low concentrations of the two kinds of atoms make the probability of such a transition extremely slight.

[4] Geiger and Scheel, "Handbuch der Physik," Springer, Berlin, **1926**, Vol. IX, p. 399.

[5] Wien, *Ann. Physik*, **83,** 1 (1927).

[6] Kerschbaum, *ibid.*, **83,** 287 (1927).

constant to decrease rapidly as the pressure of the other molecules was reduced below 1 mm.

In the particular reaction under consideration the active form of the chlorine must react either with water or hydrogen. For reasons which will be given later the reaction with water seems to be the more probable, but since it is not definitely established the effect of varying both the hydrogen and water vapor pressures must be considered. Coehn and Jung[7] found that the rate of the reaction is independent of the pressure of water vapor down to 10^{-5} mm. It follows immediately that if the first step in the chain mechanism is a reaction between the active chlorine and a water molecule, the active form of the chlorine cannot be an excited molecule, as the life period of such a molecule would be very much shorter than the time between collisions with water molecules. It remains to be shown that the same is true if the active chlorine reacts with a hydrogen molecule.

In order to make the effect of diminishing pressure on the rate easy to detect, it is desirable to have the rate equation as simple as possible. From the work on the reaction between H_2 and Cl_2 at high pressures, we know that if the chlorine is much in excess the reaction follows the law

$$\frac{d(HCl)}{dt} = -2\frac{d(H_2)}{dt} = KI_0(H_2)(Cl_2)$$

By keeping the Cl_2 pressure constant or putting in so much chlorine that the change in pressure may be neglected, this equation may be integrated to give

$$\log (H_2) = -Kt + a$$

where K includes the chlorine pressure, the light intensity and any numerical constants, and a is the constant of integration. Now if we are dealing with active molecules, K will not be constant as the pressure is lowered, whereas if the chlorine is dissociated it will be constant over the entire pressure range down to 0.001 mm. pressure of H_2 and probably lower, although the accuracy of the measurements decreases rapidly at lower pressures.

Experimental

The reaction was studied by illuminating the mixture of the moist gases in a pyrex glass bulb of about 300 cc. capacity with white light from a 100-watt tungsten filament lamp placed about 2 cm. from the reaction chamber. At intervals the chlorine and hydrochloric acid were frozen out with liquid air and the pressure of the residual hydrogen was measured by means of a modified Pirani gage which had only glass exposed to the reaction mixture.[8]

The hydrogen, prepared electrolytically from a potassium hydroxide solution, was passed over hot copper to remove oxygen, then over phosphorus pentoxide, and through a liquid-air trap into the apparatus.

The chlorine was prepared by two different methods. First, it was prepared by

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[7] Coehn and Jung, *Z. physik. Chem.*, **110**, 705 (1924).

[8] Rollefson, THIS JOURNAL, **51**, 804 (1929).

treating maganese dioxide with hydrochloric acid and washing the liberated chlorine with water and concentrated sulfuric acid, and then condensing for introduction into the apparatus. The second method was to heat anhydrous cupric chloride. In both cases the chlorine was distilled at least once in a high vacuum and was introduced into the reaction bulb at its own vapor pressure at the melting point of ether or methyl alcohol, depending on the conditions desired. In some experiments the chlorine pressure of Cl_2 was kept constant during the experiment by leaving the reaction chamber connected to the supply of chlorine in the freezing bath. In the other experiments the pressure of hydrogen used was so small compared to the chlorine pressure that the chlorine supply could be sealed off without making the percentage change in the chlorine pressure very large. The vapor pressure of the chlorine at the melting point of ether as interpolated from data in the Landolt-Börnstein "Tabellen" is 1.4 mm. The value at the melting point of methyl alcohol is obtained from Harteck's data[9] as 13.7 mm.

TABLE I

DATA FOR A TYPICAL RUN

Reaction vessel filled with chlorine at vapor pressure at melting point of ether (−116°). Pressure of chlorine, 1.4 mm. Chlorine supply sealed off before experiment. Temperature, 24.8°.

t, min.	Gage reading	Press. of H_2, mm.	Log p	t, min.	Gage reading	Press. of H_2, mm.	Log p
0	1040	0.078	−1.108	256	793	0.0195	−1.710
31	998	.066	−1.180	401	739	.0080	−2.097
106	910	.045	−1.347	461	728	.0055	−2.260
166	855	.032	−1.495	609	712	.0018	−2.745
196	830	.0275	−1.561	692	707	.0007	−3.155
				1400	704	.0000	.....

These results are plotted in Fig. 1. From the straight line obtained for the log p-t plot, we may conclude that there is no change in the rate constant as the pressure of H_2 is diminished. The slight curvature in the region of low pressures can be attributed to a small error in the zero reading of the gage. The value for $d(\log p)/dt$ in this case is −0.144, using the pressure in mm. and time in hours. In ten other experiments, six being with the chlorine reservoir in a freezing bath of melting ether left connected to the reaction vessel, the slope did not vary from this by more than a factor of two.

In order to find the effect of varying the chlorine pressure, runs were made at the two pressures previously mentioned. As the sensitivity of H_2 and Cl_2 is not the same for all mixtures, the reaction vessel was left connected to the source of chlorine and the rate constant determined with the chlorine at the melting point of ether, then at the melting point of methyl alcohol and then again at the melting point of ether using one filling of H_2. The ratio of the rates was found to be about 10 ± 1 in four experiments, which is the same as the ratio of the pressures, so we may conclude that the rate equation at low pressures with excess chlorine remains

$$-\frac{d(H_2)}{dt} = KI_0(Cl_2)\,(H_2)$$

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[9] Harteck, *Z. physik. Chem.*, **134**, 21 (1928).

Theoretical

The results have shown that whether we consider that the active form of chlorine reacts with H_2O, H_2 or Cl_2, this active form must have a life period considerably longer than has been found for any optically excited states. It follows that the chlorine molecule must be dissociated by the light presumably, according to Franck's theory, into a normal atom and one in the $^2P_1$ state. The next stage in the problem is to decide whether one or both of these start the reaction chain and what the first step in this chain is. Since we have no HCl formed by visible light if the gases are carefully dried, we may conclude that water enters into the reaction chain before any HCl is formed. It can have no effect on the initial absorption process since it has been shown by Kornfeld and Steiner[10] that moist and dry chlorine have identical absorption spectra. Assumption of an addition product with water which has too small an absorption to be noted is invalid since the concentration of such a complex, and therefore the reaction rate, should be dependent on the water vapor pressure up to a much higher pressure than the experimentally found 10^{-5} mm. It follows that one or both of the atoms formed by the action of the light must react with water to start the chain process. The most probable type of reaction is the formation of an addition compound, $Cl \cdot H_2O$, since any other reaction such as $Cl + H_2O = HCl + OH$ might be expected to be followed by reactions which would result in oxygen being formed, and there is no evidence for such a step. Furthermore, the nature of the effect of the water-vapor pressure on the reaction rate indicates that it is the chlorine atom

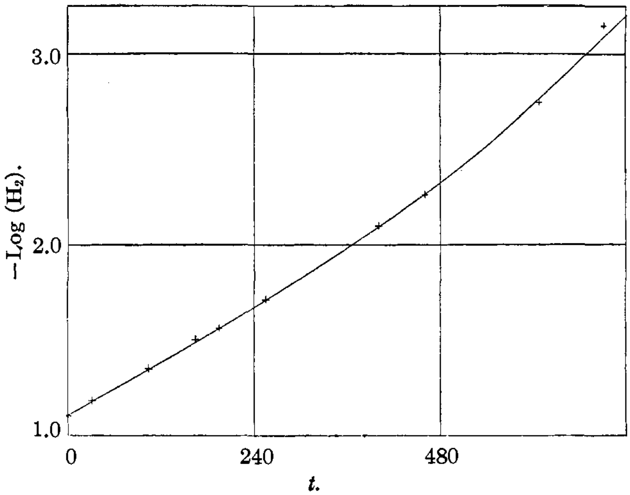

Fig. 1.

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[10] Kornfeld and Steiner, *Z. Physik*, **45**, 325 (1927).

in the $^2P_1$ state which reacts. If it were a normal atom which reacted, the rate should depend on the relative number of water molecules and chlorine atoms, which means that under a given set of conditions the rate should be approximately linearly proportional to the water-vapor pressure. On the other hand, if it is the activated atom which reacts, the number remaining in the active state long enough to react with a water molecule falls off exponentially as the water-vapor pressure is decreased. This is in accord with the experiments of Coehn and Jung.[7] Using their data the life period of the metastable state of chlorine may be estimated to be about two hundredths of a second, which is a reasonable value.

Starting in this way we may build up the following series of reactions

$$Cl_2 + h\nu = Cl + Cl(^2P_1) \qquad (1)$$
$$Cl(^2P_1) + H_2O = Cl{\cdot}H_2O \qquad (2)$$
$$Cl{\cdot}H_2O + H_2 = HCl + H_2O + H \qquad (3)$$
$$H + Cl_2 = HCl + Cl(^2P_1) \qquad (4)$$

The chain may be terminated by such reactions as

$$Cl{\cdot}H_2O + Cl = Cl_2 + H_2O \qquad (5)$$
$$Cl(^2P_1) + Cl = Cl_2 + h\nu \qquad (6)$$
$$H + H = H_2 \qquad (7)$$
$$Cl + Cl = Cl_2 \qquad (8)$$
$$H + Cl = HCl \qquad (9)$$

With low hydrogen pressures (5), (6) and (8) will be the limiting reactions, whereas with low chlorine pressures Reaction (7) may play an important role.

The observed reaction rate is determined by the number of reaction chains started and the length of these chains. The number of chains which are started will depend on the number of $Cl(^2P_1)$ atoms formed by the absorption of light which react according to (2) before they lose their activation by collision. In ordinary moist gases (2) is very fast, so that (1) becomes the determining reaction for the number of chains started. For small absorption of light the rate for (1) becomes

$$\left(\frac{d[Cl(^2P_1)]}{dt}\right)_1 = k_1 I_0 (Cl_2)$$

where k_1 is a constant including such factors as the absorption coefficient and thickness of the absorbing layer. I_0 is the intensity of the incident light.

The other factor in determining the observed reaction rate, the length of the chains, is determined by the preponderance of (3) and (4) over the reactions (5) to (9). In the experiments described in this paper we have found that the reaction rate is proportional to the hydrogen pressure if the chlorine pressure and light intensity are constant. This may be interpreted by saying that the length of the reaction chains is determined by the extent that (3) predominates over (5), as (4) under these conditions is one of the fast reactions of the system. At high hydrogen pressures (3) becomes fast and (4) is the rate-determining reaction. From these conditions we obtain the limiting rate laws (1) for excess chlorine

$$\frac{d(HCl)}{dt} = kI_0(Cl_2)(H_2)$$

and (2) for excess hydrogen

$$\frac{d(HCl)}{dt} = kI_0(Cl_2)^2$$

Several writers have attempted to give derivations of these equations based on the mechanisms they have proposed. In these derivations it has been common practice to calculate steady state concentrations of such intermediate substances as chlorine atoms, hydrogen atoms and various active molecules. In view of the fact that we have very little information concerning the factors influencing the existence of such substances in a gas mixture, such calculations require the introduction of so many assumptions that they must be considered extremely approximate. We shall take the stand that it is unnecessary to consider these steady state concentrations, but instead we shall say that each step in the mechanism is to be considered as having a group of side reactions associated with it. If a particular step is one of the rate-determining steps, then these side reactions proceed with a rate comparable with the main reaction. Thus when we have excess chlorine we have said that the rate is determined by the predominance of (3) over (5), but there may be other unknown side reactions as well. The net result, however, is such that if we consider the conditions favoring the side reactions involving $Cl{\cdot}H_2O$ as constant, then the relative number of $Cl{\cdot}H_2O$ molecules reacting with H_2 and entering into side reactions is determined by the pressure of H_2.

In the intermediate region the rate equation as given by Thon (omitting the factor due to oxygen) is

$$\frac{d(HCl)}{dt} = \frac{kI_0(Cl_2)^2(H_2)}{k'(H_2) + k''(Cl_2)}$$

This equation may also be explained on the basis of the proposed mechanism. The numerator of the right-hand member of the above equation has the form given, since the rate depends on the amount of light absorbed and on Reactions 3 and 4. The denominator is due to the fact that the chain-terminating reactions, 7 to 9, require triple collisions in order to dispose of the energy of reaction, and therefore their rates will depend on the total pressure, thus making the rate of formation of HCl inversely proportional to the total pressure, that is, to $(H_2) + (Cl_2)$. Since the hydrogen and chlorine molecules are not equally efficient in removing the reaction energy in these triple collisions, the coefficients of the two terms in this sum will not be identical; hence we find the coefficients k' and k'' in the rate equation. This effect due to the total pressure in the system would ultimately reduce the rate equation to the simple limiting forms which have been given, but is scarcely sufficient to account for these simple forms holding over as wide a range as they do. However, when we introduce the additional condition that (3) shall be the principal rate-determining reaction at low hydrogen pressures and (4) at high hydrogen pressures, we see that the two effects aid each other in reducing the rate equation to the simple forms, so that it is to be expected that the more complex form will be required only in a rather narrow range. This range will be determined by the relative values of the rate constants for (3) and (4) and the coefficients k' and k''. Experimentally it has been found to lie between $(H_2) > {}^1/_4(Cl_2)$ and $(H_2) < 2(Cl_2)$, the upper limit being somewhat uncertain.

Another point for discussion is the assumption in (4) that the chlorine atom formed by that reaction is in the $^2P_1$ state. This assumption is not necessarily true, so that formation of a normal chlorine atom in this reaction must be considered as one of the ways of terminating the chain. However, the energy of activation of the chlorine atom is so small that the atom may acquire this activation by collision as the HCl molecule and Cl atom fly apart. Whether the $Cl(^2P_1)$ is formed directly or by collision, the ultimate result may be considered as corresponding to (4).

In comparing the mechanism proposed in this paper with others which have been proposed, it is to be noted that the principal change made is the introduction of water into the reaction chain. This point has already been discussed. With regard to other features of mechanism, an interesting one is the assumption made by Cremer[11] that the reaction chain involves the formation of Cl_3. She disregards the role of water in setting up her mechanism, but otherwise she is able to account for the observed rate equations. The experimental data available are insufficient to decide whether Cl_3 is formed in the chain or not, but some experiments have been planned which it is hoped will throw some light on this point. If such a mechanism should be adopted, water would enter the chain prior to the formation of Cl_3.

One objection which has been raised against the atomic chain mechanism is that all the experiments which have been tried in which the chlorine has been illuminated and then mixed with hydrogen have failed to show the formation of hydrochloric acid, although the time between illumination of the chlorine and its mixing with hydrogen has been less than the life period of the $Cl(^2P_1)$ as calculated in this paper. These experiments have been tried in narrow tubes and under such conditions that it is quite likely that the $Cl(^2P_1)$ atoms are deactivated by collisions with the walls as they are swept through the tube in a much shorter time than would

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[11] Cremer, *Z. physik. Chem.*, **128,** 285 (1927). See also Göhring, *Z. Elektrochem.*, **27,** 511 (1927).

be the case if they were left in the middle of a large volume of gas. Before such experiments can be considered as being definitely against an atomic chain theory, it must be established that chlorine atoms could survive under the experimental conditions used long enough to get mixed with the hydrogen.

So far no account has been taken of the various substances which act as inhibitors for this reaction. The only one which has been studied quantitatively is oxygen, in which case it has been found that the rate of formation of hydrochloric acid is roughly inversely proportional to the pressure of the oxygen. In the proposed mechanism the oxygen could diminish the rate of formation of HCl by removal of the hydrogen atoms or by deactivating the $Cl(^2P_1)$; in other words, it diminishes the length of the chain. The magnitude of this effect is proportional to the oxygen pressure which makes the length of the chains and therefore the rate of the reaction inversely proportional to the oxygen pressure. This proportionality will hold only as long as the oxygen is one of the principal causes for the termination of the reaction chain. At very low oxygen pressures the other factors influencing the length of the chain predominate and the oxygen effect becomes negligible.

Summary

The photosynthesis of hydrochloric acid has been studied at low pressures with excess chlorine and has been found to follow the rate law

$$\frac{d(HCl)}{dt} = kI_0(H_2)(Cl_2)$$

From these experiments and the work of other observers it is concluded that the action of light on this reaction is to form chlorine atoms in the $^2P_1$ state which serve as the starting point for the reaction chain. A mechanism is formulated which accounts for the action of water in this system and is in accord with the observed rate equations.

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