ing law predicts a value of $-\log f = 0.319$ in the 0.1 M solvents, and the last column gives the values of the parameter "a" in Å. units required by this theory. The values of "a" are absurdly small for the nitrates, which is frequently the case, but are actually negative in the case of chlorides, which is unusual for low valence chloride salts in water.

Summary

The solubility of lead iodate is $3.61 \cdot 10^{-5}$ mole/liter at 25°. The greater solubility in 0.1 N chlorides than in the nitrates of sodium and potassium is attributed to complex chloride formation.

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THE EFFECT OF IODINE CHLORIDE ON THE PHOTOSYNTHESIS OF HYDROCHLORIC ACID

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In recent discussions of the mechanism of the photosynthesis of hydrochloric acid it has been generally accepted that the action of the light which initiates the chain is to dissociate a chlorine molecule into a normal chlorine atom and one excited to the $^2P_1$ state. A recent paper by Rollefson[1] discussed grounds for believing that it is the excited atoms which start the reaction, the normal ones having no effect. It is highly desirable, therefore, to carry out experiments in which only one of the two kinds of atoms is produced and to see if the reaction will start under such conditions. For such experiments to be of significance it is necessary that the atoms shall be produced with as little disturbance to the other molecules as possible. The most obvious way to do this is to dissociate some molecule by light. In this case it is possible to do it by introducing iodine monochloride into the mixture of hydrogen and chlorine and it is the purpose of this paper to present experiments dealing with the behavior of such a system.

The absorption spectrum of iodine chloride has been studied by Gibson and Ramsperger,[2] who found a series of bands converging at $\nu = 17{,}410$ cm.$^{-1}$ ($\lambda = 5744$ Å.) similar in character to the bands which have been observed in the halogens by Mecke[3] and Kuhn.[4] In the case of the halogens it was shown that the convergence corresponded to a dissociation into a normal and an excited atom. The thermal data available for iodine chloride are not sufficiently accurate to say definitely whether the observed convergence corresponds to a dissociation into two normal atoms or into a

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[1] Rollefson, THIS JOURNAL, **51**, 770 (1929).

[2] Gibson and Ramsperger, *Phys. Rev.*, **30**, 598 (1927).

[3] Mecke, *Ann. Physik*, **71**, 104 (1923).

[4] Kuhn, *Z. Physik*, **39**, 77 (1926).

normal iodine atom and an excited chlorine atom. Gibson and Ramsperger adopted the first of these two interpretations, their arguments being based on considerations of the stability of iodine chloride and also on the observation of two faint band heads at higher frequencies than the above-mentioned convergence which might be considered as part of a system corresponding to the second process. Gibson[5] later abandoned this view in favor of the dissociation into a normal iodine atom and excited chlorine atom. Whichever interpretation is correct, the fact that there is one well-defined band series in the absorption indicates that this compound can be used to supply one kind of chlorine atoms.

Preliminary experiments showed that no reaction occurred if a mixture of iodine chloride and hydrogen was illuminated at room temperature. This result tells us merely that the kind of chlorine atoms obtained in these experiments will not react directly with hydrogen. It does not exclude the possibility of these atoms starting chains by going through a Cl_3 stage, as postulated by Cremer,[6] if chlorine molecules are present. The principal experiments were therefore performed with mixtures of chlorine, iodine chloride and hydrogen.

Experimental

The reaction was carried out in a cylindrical pyrex vessel, 6 × 17.5 cm., with a polished window at one end; the other end was drawn down and sealed to a smaller tube in order that the vessel might easily be attached to the line, and a side tube of approximate dimensions 1 × 13 cm. was sealed onto the vessel at about the middle. The purpose of the side tube was to freeze out such gases as hydrochloric acid, chlorine, etc., in order that the pressure of hydrogen might be measured and the reaction followed in this way. Liquid air was used to freeze out the above-mentioned gases and a manometer containing concentrated sulfuric acid was used to measure the pressure of hydrogen. The manometer was so arranged that, during the addition of the reacting substances to the vessel, its high vacuum side could be cut off from the main line by means of a pyrex stopcock. In order to assure the maintenance of a high vacuum on this side of the manometer after the addition of the reactants, the stopcock was opened, thereby allowing the high vacuum side of the manometer to be continually pumped on by a mercury diffusion pump which was backed up by an oil pump. Before admitting the reacting gases to the vessel, the entire system was evacuated by means of the above-mentioned pumping system. The hydrogen used was prepared by the electrolysis of a concentrated solution of potassium hydroxide. The gas, after being generated, was passed over metallic copper at a temperature of approximately 300° in order to remove any oxygen that might have been present, then over phosphorus pentoxide, then through a liquid air trap to a U in the line surrounded by a mixture of solid carbon dioxide and acetone, and from this U through a capillary tube into the reaction vessel. The capillary tube was placed in the line between the U, surrounded by the solid carbon dioxide–acetone mixture, and the reaction vessel in order to prevent the iodine chloride from diffusing from the reaction vessel to the cold U during the experimental work. During the addition of hydrogen the side tube was surrounded with liquid air and the pressure of hydro-

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[5] Gibson, *Z. Physik.*, **50**, 692 (1928); Gibson and Rice, *Nature*, **123**, 347 (1929).

[6] Cremer, *Z. physik. Chem.*, **128**, 285 (1927).

gen added was taken as the initial hydrogen pressure reading. The liquid air was then removed and chlorine was admitted to the reaction vessel. The chlorine was prepared by heating anhydrous cupric chloride, which was kept in a tube sealed on the line between the liquid-air trap and the solid carbon dioxide–acetone U. In this way the chlorine passed through the cold U, through the capillary tube, into the reaction vessel. The iodine chloride was prepared by direct reaction of iodine and chlorine in the reaction vessel. The iodine used was sublimed twice and then condensed in small tubes which had been drawn off to a fine capillary. After the iodine was condensed, the tubes were sealed off and laid aside for use. When iodine was to be introduced into the reaction vessel, one of these tubes was placed in a side tube where it could be broken by a magnetic hammer. The iodine was allowed to distil into the reaction vessel. In this way, the iodine was resublimed three times and a pure product was assured. When sufficient iodine had been introduced into the vessel, the magnetic hammer arrangement was sealed off and hydrogen and chlorine were introduced into the vessel. This mixture of gases was exposed to the light for a period of an hour or longer; then the side tube was surrounded by liquid air, and the gases, with the exception of hydrogen, were frozen out. The liquid air was then replaced by a mixture of solid carbon dioxide–acetone, which allowed the chlorine and hydrochloric acid to evaporate, keeping the iodine chloride in the solid state as iodine trichloride. The gases were pumped off and the system again evacuated. Hydrogen and chlorine were again added, in the manner previously described, and a series of measurements was made. The vessel was illuminated by means of a 500-watt projection lamp, the light from which was concentrated by a lens and passed through a quinine sulfate filter onto the plane window. The gases were exposed to the light for a definite length of time and then the amount of hydrochloric acid formed was determined by freezing out the gases and measuring the pressure of residual hydrogen. The rate of the reaction was followed by taking a series of such measurements. The iodine chloride pressure was varied by pumping out a certain fraction of the total gases and then adding hydrogen and chlorine to the remaining gases until approximately the original pressures of hydrogen and chlorine were reached. A series of points was again obtained, as described above, and by making a series of such runs, the effect of iodine chloride on the rate of the reaction between hydrogen and chlorine was studied.

In all the experiments a large excess of chlorine was used so that no large error was introduced by considering the chlorine pressure as constant during the run. Under such conditions the law for the rate of formation of hydrochloric acid is

$$\frac{\mathrm{d}(\mathrm{HCl})}{\mathrm{d}t} = k(\mathrm{Cl_2})(\mathrm{H_2}) = k'(\mathrm{H_2}) = -\frac{1}{2}\frac{\mathrm{d}(\mathrm{H_2})}{\mathrm{d}t}$$

where $k' = k(\mathrm{Cl_2})$. Integrating we find that log $(\mathrm{H_2})$ should be proportional to the time; therefore if we plot log $(\mathrm{H_2})$ against time the slope of the curve gives us the value of k'. A set of curves obtained at various iodine chloride pressures[7] is shown in Fig. 1. The straightness of the lines shows the validity of the assumptions over the range studied. The variation of k' with the iodine chloride pressure is shown in Fig. 2, where values of k' have been plotted against the square root of the reciprocal of the pressure of iodine chloride. This was found, by trial, to be the best linear plot which could be obtained, although even in this case the deviations are

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[7] The pressure unit is cm. of sulfuric acid.

fairly large at low pressures. Such deviations are not surprising, as at low pressures there is apt to be considerable uncertainty in the iodine chloride pressure. The general reproducibility of the results is shown by the fact that the points used in making this graph are from two different sets of runs; the dots are from one series and the circles from the other.

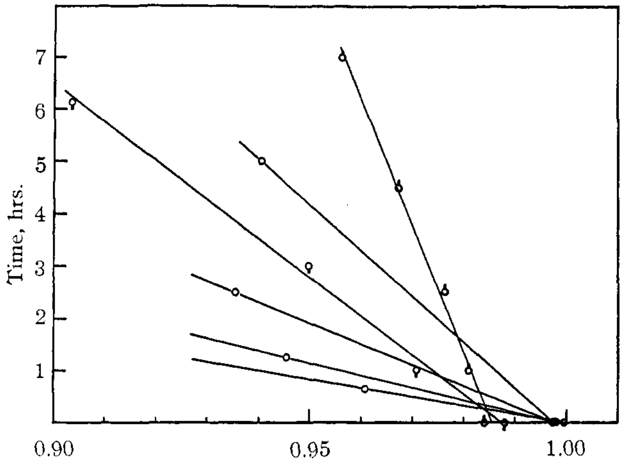

Fig. 1.

All these runs were made using the quinine sulfate filter, which cuts off all wave lengths shorter than 4050 Å. Another run was made using a piece of Corex Red Purple glass as a filter. This transmits the ultraviolet and also some light between 4000 and 4500 Å. The reaction occurred at a measurable rate, although it was somewhat slower than that with the

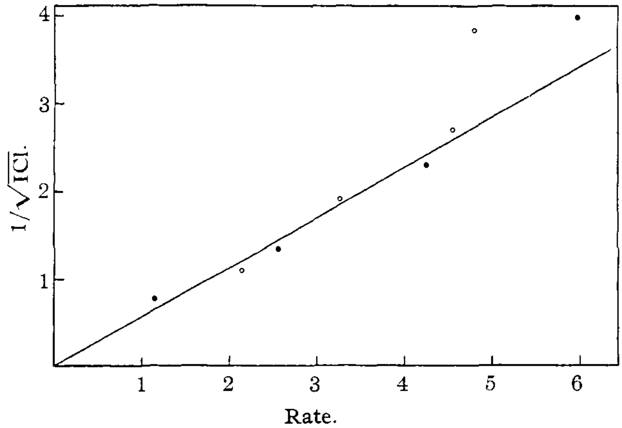

Fig. 2.

quinine sulfate filter, as might be expected due to lower intensity of the light source in the ultraviolet. Another run was made using a Wallace filter No. 8 which transmits between 4300 and 5600 Å.,[8] but in this case no reaction was observed, even with long exposures, although the light absorbed by the iodine chloride in this case was greater than that absorbed by the chlorine in the test with the Corex filter.

Discussion of Results

From the experiments which have just been described we can conclude that it is not possible to bring about the formation of hydrochloric acid by the optical dissociation of iodine monochloride in hydrogen, either in the presence or absence of chlorine molecules. Furthermore, if we have a mixture of the three substances and illuminate with light which is absorbed by chlorine, a reaction occurs, but at a much slower rate than if no iodine chloride is present. This may seem to be in direct contradiction to the results published by Padoa,[9] who reported that the formation of hydrochloric acid was accelerated by the addition of iodine. His experiments, however, were carried out using an actinometer in which water was present, and it is well known that under such circumstances the chlorine would oxidize the iodine to iodate, so it is very unlikely that he had any appreciable amount of any iodine compound in the gas phase.

Let us consider the first conclusion above from the standpoint of the two interpretations which have been given to the absorption spectrum of iodine chloride. If the interpretation given most recently by Gibson is correct, *i. e.*, the molecule is dissociated into a normal iodine atom and an excited chlorine atom, it is difficult to see why we should fail to observe the formation of hydrochloric acid. Regardless of whether the chains in the hydrochloric acid reaction are started by normal or activated atoms under ordinary circumstances, if we introduce the atoms in the higher state, they must start a reaction either at once or as soon as they have been brought to the normal state, which would be a matter of frequent occurrence at the pressures used. On the other hand, if the original interpretation of Gibson and Ramsperger is correct, and normal atoms are formed in the optical dissociation of iodine chloride, the number of chlorine atoms in the first excited state, the $^2P_1$ state, would be very small, as the average kinetic energy of molecules at room temperature is not sufficient to cause any appreciable fraction of the atoms to be in the higher state. If, under such circumstances, the reaction with hydrogen requires the activated atom, then we should expect just what was actually observed, namely, no formation of hydrochloric acid. From the experiments which we have

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[8] The amount of reaction which would be caused under these conditions by the absorption of light in this region by the chlorine is negligible.

[9] Padoa, *Gazz. chim. ital.*, **51**, I, 193 (1921).

described it is, therefore, possible for us to conclude definitely, first, that visible light of wave lengths less than 5744 Å. dissociates iodine chloride into two normal atoms; second, the reaction chains in the formation of hydrochloric acid are started by chlorine atoms in the ${}^2P_1$ state and not by the normal atoms. It remains undetermined whether or not the chain goes through a Cl_3 stage.

With regard to the inhibiting effect of iodine chloride on the reaction, it is much easier to give a qualitative picture than to account for the quantitative result. Among the more probable explanations would be the reduction of the concentration of chlorine atoms in the ${}^2P_1$ state due to collisions with iodine chloride being very efficient in bringing about a return to the normal state. Or we may have reactions such as

$$\mathrm{Cl^* + ICl = Cl_2 + I}$$
$$\mathrm{H + ICl = HCl + I}$$

Either of these would terminate the chain since the iodine atoms do not react with hydrogen. The iodine atoms would eventually be converted into iodine chloride. Such reactions would be expected to cause an inhibiting action proportional to the first power of the iodine chloride pressure, whereas the observed effect was definitely less. The explanation of the discrepancy is not apparent, but it may be that other apparatus which will be capable of studying the reaction over a wider range of conditions will be able to produce a key to the solution.

Summary

The photochemical formation of hydrochloric acid in the presence of iodine chloride has been studied at room temperature. From the experimental data obtained it has been shown that the following conclusions may be drawn.

1. Iodine chloride is dissociated into normal atoms by the action of light of wave length less than 5744 Å.
2. The formation of hydrochloric acid requires the presence of chlorine atoms in the ${}^2P_1$ state.
3. The rate of formation of hydrochloric acid by light of wave length greater than 4050 Å. is inversely proportional to the square root of the iodine chloride pressure.

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