

On two new compounds of chlorine and carbon, and on a new compound of iodine, carbon, and hydrogen / [Michael Faraday].

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Mr. Faraday
presented to the

ON

TWO NEW COMPOUNDS OF CHLORINE
AND CARBON,

AND ON

A NEW COMPOUND OF IODINE, CARBON,
AND HYDROGEN.

BY

MR. FARADAY,

Chemical Assistant in the Royal Institution.

FROM THE

PHILOSOPHICAL TRANSACTIONS.

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By Order of the President and Council,

W. T. BRANDE, Sec. R. S.

ON TWO NEW COMPOUNDS, &c.

Read before the ROYAL SOCIETY, December 21, 1820.

ONE of the first circumstances that induced Sir H. DAVY to doubt the compound nature of what was formerly called oxymuriatic acid gas, was the want of action of heated charcoal upon it; and considerable use of the same agent, and of the phenomena exhibited by it in different circumstances with chlorine, was afterwards made in establishing the simple nature of that body.

The true nature of chlorine being ascertained, it became of importance to form all the possible compounds of it with other elementary substances, and to examine them in the new view had of their nature. This investigation has been pursued with such success at different times, that very few elements remain uncombined with it; but with respect to carbon, the very circumstance which first tended to correct the erroneous opinions which, after SCHEELÉ's time, and before the year 1810, had gone abroad respecting its nature, proved an obstacle to the formation of its compounds; and up to the present time, the chlorides of carbon have escaped the researches of chemists.

That the difficulty met with in forming a compound of chlorine and carbon, was probably not owing to any want of

weakness of affinity between the two bodies, was pointed out by Sir H. DAVY; who, reasoning on the triple compound of chlorine, carbon, and hydrogen, concluded that the attraction of the two bodies for each other was by no means feeble; and the discovery of phosgene gas by Dr. DAVY, in which chlorine and carbon are combined with oxygen, was another circumstance strongly in favour of this opinion.

I was induced last summer to take up this subject, and have been so fortunate as to discover two chlorides of carbon, and a compound of iodine, carbon, and hydrogen, analogous in its nature to the triple compound of chlorine, carbon, and hydrogen, sometimes called chloric ether. I shall endeavour in the following pages to describe these substances, and give the experimental proofs of their nature.

If chlorine and olefiant gas be mixed together, it is well known that condensation takes place, and a colourless limpid volatile fluid is produced, containing chlorine, carbon, and hydrogen. If the volumes of the two gases are equal, the condensation is perfect. If the olefiant gas is in excess, that excess is left unchanged. But if the chlorine is in excess, the fluid becomes of a yellow tint, and acid fumes are produced. This circumstance alone proves, that chlorine can take hydrogen from the fluid; and on examination, I found it was without the liberation of any carbon or chlorine.

That the action thus began, might be carried to its utmost extent, some of the pure fluid (chloric ether) was put into a retort with chlorine, and exposed to sunshine. At the first instant of contact between the chlorine and the fluid, the latter became yellow; but when in the sun's rays, a few moments sufficed to destroy the colour both of the fluid and the chlorine,

heat being at the same time evolved. On opening the retort, there was no absorption, but it was found full of muriatic acid gas. This was expelled, and more chlorine introduced, and the whole again exposed to sun light: the colour again disappeared, and a few moist crystals were formed round the edge of the fluid. Chlorine being a third time introduced, and treated as before, it still removed more hydrogen; and now a sublimate of crystals lined the retort. Proceeding in this way until the chlorine exerted no farther action, the fluid entirely disappeared, and the results were, the dry crystalline substance, and muriatic acid gas.

A portion of olefiant gas was then mixed in a retort with eight or nine times its bulk of chlorine, and exposed to sun light. At first the fluid formed; but this instantly disappeared; the retort became lined with crystals, and the colour of the chlorine very much diminished.

On examining these crystals, I found they were the compound I was in search of; but before I give the proofs of their nature, I will describe the process by which this chloride of carbon can be obtained pure.

Perchloride of carbon.

A glass vessel was made in the form of an alembic head, but without the beak; the neck was considerably contracted, and had a brass cap with a stop-cock cemented on; at the top was a small aperture, into which a ground stopper fitted air tight. The capacity of the vessel was about 200 cubic inches. Being exhausted by the air-pump, it was nearly filled with chlorine; and being then placed over olefiant gas, and as much as could enter having passed in, the stop-cocks

were shut, and the whole left for a short time. When the fluid compound of chlorine and olefiant gas had formed and condensed on the sides of the vessel, it was again placed over olefiant gas, and, in consequence of the condensation of a large portion of the gases, a considerable quantity more entered. This was left, as before, to combine with part of the remaining chlorine, to condense, and to form a partial vacuum; which was again filled with olefiant gas, and the process repeated until all the chlorine had united to form the fluid, and the vessel remained full of olefiant gas. Chlorine was then admitted in repeated portions as before; consequently, more of the fluid formed; and ultimately a large portion was obtained in the bottom of the vessel, and an atmosphere of chlorine above it. It was now exposed to sun light. The chlorine immediately disappeared, and the vessel became filled with muriatic acid gas. Having ascertained that water did not interfere with the action of the substances, a small portion was admitted into the vessel which absorbed the muriatic acid gas, and then another atmosphere of chlorine was introduced. Again exposed to the light, this was partly combined with the carbon, and partly converted into muriatic acid gas; which, being as before absorbed by the water, left space for more chlorine. Repeating this action, the fluid gradually became thick and opaque from the formation of crystals in it, which at last adhered to the sides of the glass as it was turned round; and ultimately the vessel only contained chlorine with the accumulated gaseous impurities of the successive portions; a strong solution of muriatic acid, coloured blue from the solution of a little brass, and the solid substance.

I have frequently carried the process thus far in retorts;

and it is evident, that any conveniently formed glass vessel will answer the purpose. The admission of water during the process prevents the necessity of repeated exhaustion by the air-pump, which cannot be done without injury to the latter; but to have the full advantage of this part of the process, the gases should be as pure as possible, that no atmosphere foreign to the experiment may collect in the vessel.

In order to cleanse the substance, the remaining chlorine and muriatic acid were blown out of the vessel by a pair of bellows, introduced at the stoppered aperture, and the vessel afterwards filled with water, to wash away the muriatic acid and other soluble matters. Considerable care is then requisite in the farther purification of the chloride. It retains water, muriatic acid, and a substance, which I find to be a triple compound of chlorine, carbon, and hydrogen, formed from the cement of the cap; and as all these contain hydrogen, a small quantity of any one remaining with the chloride would, in analysis, give erroneous results. Various methods of purification may be devised, founded on the properties of the substance, but I have found the following the most convenient. The substance is to be washed from off the glass, and poured with the water into a jar; a little alcohol will remove the last portions which adhere to the glass; and this when poured into the water will precipitate the chloride, and the whole will fall to the bottom of the vessel. Then having decanted the water, the chloride is to be collected on a filter, and dried as much as may be by pressure between folds of bibulous paper. It should next be introduced into a glass tube, and sublimed by a spirit lamp: the pure substance with water will rise at first, but the last portions will be partially decom-

posed, muriatic acid will be liberated, and charcoal left. The sublimed portion is then to be dissolved in alcohol, and poured into a weak solution of potash, by which the substance is thrown down, and the muriatic acid neutralized and separated: then wash away the potash and muriate by repeated affusions of water, until the substance remains pure; collect it on a filter, and dry it, first between folds of paper, and afterwards by sulphuric acid in the exhausted receiver of the air-pump.

It will now appear as a white pulverulent substance; and if perfectly pure, will not, when a little of it is sublimed in a tube, leave the slightest trace of carbon, or liberate any muriatic acid. A small portion of it dissolved in ether, should give no precipitate with nitrate of silver. If it be not quite pure, it must be re-sublimed, washed, and dried until it is pure.

This substance does not require the direct rays of the sun for its formation. Several tubes were filled with a mixture of one part of olefiant gas with five or six parts of chlorine, and placed over water in the light of a dull day; in two or three hours there was very considerable absorption, and crystals of the substance were deposited on the inside of the tubes. I have also often observed the formation of the crystals in retorts in common day light.

A retort being exhausted, had 12 cubic inches of olefiant gas introduced, and 24.75 cubic inches of chlorine: as soon as the condensation occasioned by the formation of the fluid had taken place, 21.5 cubic inches more of chlorine were passed in, and the retort set aside in a dark place for two days. At the end of that time muriatic acid gas and the solid

chloride had formed, but the greater part of the fluid remained unchanged. Hence, it will form even in the dark, by length of time.

I tried to produce the chloride by exposure of the two gases in tubes over water to strong lamp light for two or three hours, but could not succeed.

The perchloride of carbon, when pure, is immediately after fusion, or sublimation, a transparent colourless substance. It has scarcely any taste. Its odour is aromatic, and approaching to that of camphor. Its specific gravity is as nearly as possible 2. Its refractive power is high, being above that of flint glass (1.5767). It is very friable, easily breaking down under pressure; and when scratched, has much of the feel and appearance of white sugar. It does not conduct electricity.

The crystals obtained by sublimation and from solutions of the substance in alcohol and ether, are dendritical, prismatic, or in plates; the varieties of form, which are very interesting, are easily ascertained, and result from a primitive octoëdron.

It volatilizes slowly at common temperatures, and passes, in the manner of camphor, towards the light. If warmed, it rises more rapidly, and then forms fine crystals: when the temperature is farther raised, it fuses at 320° F. and boils at 360° , under atmospheric pressure. When condensed again from these rapid sublimations, it concretes in the upper part of the tube or vessel containing it, in so transparent and colourless a state, that it is difficult, except from its high refractive power, to perceive where it is lodged. As the crust it forms becomes thicker, it splits, and cracks like sublimed camphor; and in a few minutes after it is cold, is white, and

nearly opaque. If the heat be raised still higher, as when the substance is passed through a red hot tube, it is decomposed, chlorine is evolved, and another chloride of carbon, which condenses into a fluid, is obtained. This shall be described presently.

It is not readily combustible; when held in the flame of a spirit lamp, it burns with a red flame, emitting much smoke and acid fumes; but when removed from the lamp, combustion ceases. In the combustion that does take place in the lamp, the hydrogen of the alcohol, by combining with the chlorine of the compound, performs the most important part; nevertheless, when the substance is heated red in an atmosphere of pure oxygen, it sometimes burns with a brilliant light.

It is not soluble in water at common temperatures; or only in very small quantity. When a drop or two of the alcoholic solution is poured into a large quantity of water, it renders it turbid from the deposition of the substance. It does not appear that hot water dissolves more of it than cold water.

It dissolves in alcohol with facility, and in much greater quantity with heat than without. A saturated hot solution crystallizes as it cools, and the cold solution also gives crystals by spontaneous evaporation. When poured into water, the chloride is precipitated, and falls to the bottom in flakes. If burnt, the flame of the alcohol is brightened by the presence of the substance, and fumes of muriatic acid are liberated. Solution of nitrate of silver does not produce any turbidness in it, unless it be in such quantity that the water throws down the substance; but no chloride of silver is formed.

It is much more soluble in ether than in alcohol, and more

so in hot than in cold ether. The hot solution deposits crystals as it cools; and the crystallization of a cold solution, when evaporated on a glass plate, is very beautiful. This solution is not precipitated by water, unless the ether has previously been dried, and then water occasions a turbidness. Nitrate of silver does not precipitate it. When burned, muriatic acid fumes are liberated, but the greater part of the chloride remains in the capsule.

It is soluble in the volatile oils, and on evaporation is again obtained in crystals. It is also readily soluble in fixed oils. The solutions when heated liberate muriatic acid gas, and the oil becomes of a dark colour, as if charred.

Solutions of the acids and alkalies do not act with any energy on the substance. When boiled with solutions of pure potash and soda, it rises and condenses in the upper part of the vessel; and though it be brought down to the alkali many times, and re-boiled, still the alkali, when examined, is not found to contain any chlorine, nor is any change produced. Ammonia in solution is also without action upon it. These solutions do not appear to dissolve more of it than pure water.

Muriatic acid in solution does not act at all upon it. Strong nitric acid boiled upon it dissolves a portion, but does not decompose it: as it cools, part of the chloride is deposited unaltered, and the concentrated acid, when diluted, lets more fall down. The diluted portion being filtered, and tested with nitrate of silver, gives no precipitate. It does not appear to be either soluble in, or acted upon, by concentrated sulphuric acid. It sinks slowly in the acid, and, when heated,

is converted into vapour, which, rising through the acid, condenses in the upper part of the tube.

It is not acted upon by oxygen at temperatures under a red heat. A mixture of oxygen and the vapour of the substance would not inflame by a strong electric spark, though the temperature was raised by a spirit-lamp to about 400° . When oxygen mixed with the vapour of the substance is passed through a red-hot tube, there is decomposition, and mixtures of chlorine, carbonic oxide, carbonic acid, and phosgene gases are produced. A portion of the chloride was heated with peroxide of mercury in a glass tube over mercury; as soon as the oxide had given off oxygen, and the heat had risen so high as to soften the glass considerably, the vapour suddenly detonated with the oxygen with bright inflammation. The substances remaining were oxygen, carbonic acid, and calomel; and I believe there was no decomposition or action, until so much mercury had risen in vapour as to aid the oxygen by a kind of double affinity in decomposing the chloride of carbon.

Chlorine produces no change on the substance, either by exposure to light or heat.

When iodine is heated with it at low temperatures, the two substances melt and unite, and there is no farther action. When heated more strongly in vapour, the iodine separates chlorine, reducing the perchloride to the fluid protochloride of carbon, and chloriodine is produced. This dissolves, and if no excess of iodine be present, the whole remains fluid at common temperatures. When water is added, it generally liberates a little iodine; and on heating the solution, so as to

drive off all free iodine, and testing by nitrate of silver, chloride and iodide of silver are obtained.

Hydrogen and the vapour of the substance would not inflame at the temperature of 400° F. by strong electrical sparks; but when the mixture was sent through a red hot tube, the chloride was decomposed, and muriatic acid gas and charcoal produced.

The vapour of the perchloride of carbon readily detonates by the electric spark with a mixture of oxygen and hydrogen gases; but the gaseous results are very mixed and uncertain, from the near equipoise of affinities that exist among the elements.

Sulphur readily unites to it when melted with it, and the mixture crystallizes on cooling into a yellowish mass. When heated more strongly, the substance rises unchanged, and leaves the sulphur unaltered; but when the mixed vapours are raised to a still higher temperature, chloride of sulphur and proto-chloride of carbon are formed. Sometimes there are appearances as if a carburet of sulphur were formed, but of this I have not satisfied myself.

Phosphorus at low temperatures melts and unites with the substance, without any decomposition. If heated in the vapour of the substance, but not too highly, it takes away chlorine, and forms the proto-chlorides of phosphorus and carbon. If heated more highly, it frequently inflames in the vapour with a brilliant combustion, and abundance of charcoal is deposited. Sometimes I have had the charcoal left in films stretching across the tubes, and occupying the space where the flame passed. The appearance is then very beautiful.

When phosphorus is heated with the vapour of the substance over mercury, so as not to inflame in it, there is generally a small portion of muriatic acid gas formed. If great care be taken, this is in very minute quantity; and its variable proportion sufficiently shows, that the hydrogen which forms it does not come from the substance. I am induced to believe that it is derived from moisture adhering to the phosphorus. The action of iodine on phosphorus shows, that it is very difficult to dry the latter substance perfectly.

A stick of phosphorus put into the alcoholic or ethereal solution of the perchloride did not exert any action upon it.

Charcoal heated in the vapour of the substance appears to have no action upon it.

Most of the metals decompose it at high temperatures. Potassium burns brilliantly in the vapour, depositing charcoal, and forming chloride of potassium. Iron, zinc, tin, copper and mercury, act on it at a red heat, forming chlorides of those metals, and depositing charcoal; and when the experiments are made with pure substances, and very carefully, no other results are obtained. Some of the substance was passed over iron turnings heated in a glass tube. At the commencement of the sublimation of the chloride through the hot iron, the common air of the vessels was expelled, and received in different tubes; but before one-third of the substance had been passed, all liberation of gas ceased, and the remainder was decomposed by the iron, without the production of any gaseous matters. The different portions of air that were thrown out being examined, the first proved to be common air, and the last carbonic oxide. This had resulted, probably, from the action of the chlorine on the lead of the glass tube.

An evident action had taken place, and the oxygen evolved, meeting with the liberated carbon, would produce the carbonic oxide. This experiment has been repeated several times with the same results.

When the perchloride of carbon is heated with metallic oxides, different results are produced according to the proportions of oxygen in the oxides. The peroxides, as of mercury, copper, lead, and tin, produce chlorides of those metals, and carbonic acid; and the protoxides, as those of zinc, lead, &c. produce also chlorides; but the gaseous products are mixtures of carbonic acid and carbonic oxide. I have frequently perceived the smell of phosgene gas on passing the chloride over oxide of zinc; and as the substance easily liberates chlorine at high temperatures, it will be readily seen how a small portion of that gas may be formed. It also happens, sometimes, that the protoxides become blackened from the deposition of charcoal.

When the vapour of the chloride is passed over lime, baryta, or strontia, heated red hot, a very vivid combustion is produced. The oxygen and the chlorine change places, and both the metals and the carbon are burnt. Chlorides are produced, carbonic acid is formed and absorbed by the undecomposed parts of the earths, and carbon is deposited. In these experiments no carbonic oxide is produced. When passed over magnesia, there is no action on the earth, but the perchloride of carbon is converted by the heat into protochloride.

In these experiments with the oxides no trace of water could be perceived.

Having thus far described the properties of the substance,

I shall now give the reasons which induce me to consider it a true chloride of carbon, and shall endeavour to assign its composition. My first object was to ascertain whether hydrogen existed in it, or not. When phosphorus is heated in it, a small quantity of muriatic acid is generally formed; but doubt arises as to the cause of its production, from the circumstance that the phosphorus, as already mentioned, may be the source of the hydrogen. When potassium is heated in the vapour of the substance, there is generally a small expansion of volume, and inflammable gas produced; but it is very difficult to cleanse potassium both from naphtha and an adhering crust of moist potash; and either of these, though in extremely minute quantities, would give fallacious results.

A more unexceptionable experiment made with iron, has been already described; and the inferences from it are against the presence of hydrogen in the compound.

Some of the substance in vapour was electrized over mercury, by having many hundred sparks passed through it. Calomel was formed, and carbon deposited. A very minute bubble of gas was produced, but it was much too small to interfere with the conclusions drawn respecting the binary nature of the compound; and was probably caused by air that had adhered to the sides of the tube when the mercury was poured in.

The most perfect demonstration that the body contains no hydrogen, and indeed of its nature altogether, is obtained from the circumstances which attend its formation. When the fluid compound of chlorine and olefiant gas is acted on by chlorine and solar light in close vessels, although the whole of the chlorine disappears, yet there is no change of

volume, its place being occupied by muriatic acid gas. Hence, as muriatic acid gas is known to consist of equal volumes of chlorine and hydrogen, combined without condensation, it is evident that half the chlorine introduced into the vessel has combined with the elements of the fluid, and liberated an equal volume of hydrogen; and as, when the chloride is perfectly formed, it condenses no muriatic acid gas, a method, apparently free from all fallacy, is thus afforded of ascertaining its nature.

I have made many experiments on given volumes of chlorine and olefiant gases. A clean dry retort was fitted with a cap and stop-cock. Its capacity was 25.25 cubic inches. Being exhausted by the air-pump, it was filled with nitrogen (24.25 cubic inches being required), and being again exhausted, 5 cubic inches of olefiant gas, and 10 cubic inches of chlorine were introduced. It was then set aside for half an hour, that the fluid compound might form, and afterwards being placed again over a jar of chlorine, 19.25 cubic inches entered; so that the condensation had been as nearly as possible 10 cubic inches, or twice the volume of the olefiant gas (barometer 29.1 inches). It was now placed for the day (October 18th.) in the rays of the sun; but the weather was not very fine. In the evening the solid crystalline substance had formed in abundance, and very little fluid remained. When placed over chlorine, not the slightest change in volume had been produced. The stop-cock was now opened under mercury, and a small portion of the metal having entered, it was agitated in the retort, to absorb the chlorine; the neck of the retort was left open under the mercury all night, and the whole agitated from time to time. Next morning (barometer 29.6) the mercury

which had entered, being passed into the neck of the retort, stood at a certain mark 6 inches above the level of the mercury in the trough, occupying 1.25 cubic inches, and leaving 24 cubic inches filled by the expanded muriatic acid gas and nitrogen. These volumes corrected to the pressure of 29.1 inches, give 5.78 cubic inches for the chlorine absorbed, and 19.47 cubic inches for the muriatic acid gas, &c. These absorbed by water left 1.2 cubic inches of nitrogen; so that the gases in the retort, after the action of solar light, were

Muriatic acid gas	-	18.27	cubic inches.
Chlorine	-	5.78	
Nitrogen, &c.	-	1.2	

and before that action,

Chlorine	-	29.25	cubic inches.
Olefiant gas	-	5.	
Nitrogen	-	1.	

Hence 23.47 cubic inches of chlorine had disappeared, and 9.13 of these had entered into combination with an equal volume of 9.13 cubic inches of hydrogen liberated from the 5 cubic inches of olefiant gas, to form muriatic acid; and, consequently, 14.34 cubic inches of chlorine remained combined with the carbon of the 5 cubic inches of olefiant gas. Here, the volume of chlorine actually employed is not quite five times that of the olefiant gas, nor the volume of muriatic acid gas produced, equal to four times that of the olefiant gas; but they approximate; and when it is remembered that the conversion was not quite perfect, and that the gases used would inevitably contain a slight portion of impurity, the causes of the deficiency can easily be understood.

In other experiments made in the same way, but with

smaller quantities, more accurate results were obtained. 1 cubic inch of olefiant gas with 12.25 cubic inches of chlorine, produced by the action of light 3.67 cubic inches of muriatic acid gas, 4.963 of the chlorine having been used. 1.4 cubic inch of olefiant gas with 12.5 cubic inches of chlorine produced 5.06 cubic inches of muriatic acid gas, 6.7 cubic inches of chlorine having been used. Other experiments gave very nearly the same results; and I have deduced from them, that 1 volume of olefiant gas requires 5 volumes of chlorine for its conversion into muriatic acid and chloride of carbon; that 4 volumes of muriatic acid gas are formed; that 3 volumes of chlorine combine with the 2 volumes of carbon in the olefiant gas to form the solid crystalline chloride; and that, when chlorine acts on the fluid compound of chlorine and olefiant gas, for every volume of chlorine that combines, an equal volume of hydrogen is separated.

I have endeavoured to verify these proportions by analytical experiments. The mode I adopted was, to send the substance in vapour over metals and metallic oxides at high temperatures. Considerable care is requisite in such experiments; for if the process be carried on quickly, a portion of fluid chloride of carbon is formed, and escapes decomposition. The following are two results, from a number of experiments agreeing well with each other.

5 grains were passed over peroxide of copper in an iron tube, and the gas collected over mercury; it amounted to 3.9 cubic inches, barometer 29.85; thermometer 54° F. Of these nearly 3.8 cubic inches were carbonic acid, and rather more than .1 of a cubic inch was carbonic oxide. These are nearly equal to .5004 of a grain of carbon. Hence, 100

of the chloride would give 10 of carbon nearly, but by calculation 100 should give 10.19. The difference is so small, as to come within the limits of errors in experiment.

5 grains were passed over peroxide of copper in a tube made of green phial glass, and the chlorine estimated in the same manner as before. 17.7 grains of chloride of silver were obtained equal to 4.36 grains of chlorine. This result approaches much nearer to the calculated result than the former; but there had still been action on the tube, and a minute portion of the substance had passed undecomposed, and condensed at the opposite end of the tube in crystals.

Experiments made by passing the perchloride over hot lime or barytes, promise to be more accurate and easy of performance. In the mean time, the above analytical results will perhaps be considered as strong corroboration of the opinion of the nature of the compound, deduced from the synthetical experiments; and the composition of the perchloride of carbon will be

3	proportions of chlorine	=	100.5
2	ditto	=	11.4
			111.9

Proto-chloride of carbon.

Having said so much on the nature of the perchloride of carbon, I shall have less occasion to dwell on the proofs that the compound I am about to describe, is also a binary combination of carbon and chlorine.

When the vapour of the perchloride of carbon is heated to dull redness, chlorine is liberated, and a new compound of that element and carbon is produced. This is readily shown

by heating the bottom of a small glass tube, containing some of the perchloride, in a spirit lamp. The substance at first sublimes, but as the vapour becomes heated below, it is gradually converted into proto-chloride, and chlorine is evolved.

It is not without considerable precaution that the proto-chloride of carbon can be obtained pure; for though passed through a great length of heated tube, part of the perchloride frequently escapes decomposition. The process I have adopted is the following: some of the perchloride is introduced into the closed end of a tube, and the space above it, for ten or twelve inches, filled with small fragments of rock crystal; the part of the tube beyond this is then bent up and down two or three times, so that the angles may form receivers for the new compound; then heating the tube and crystal to bright redness, and dipping the angles in water, the perchloride is slowly sublimed by a spirit lamp, and, on passing into the hot part of the tube, is decomposed; a fluid passes over, which is condensed in the angles of the tube, and chlorine is evolved: part of the gas escapes, but the greater portion is retained in solution by the fluid, and renders it yellow. Having proceeded thus far, by the careful application of a lamp and blow-pipe, the bent part of the tube may be separated from that within the furnace, and the end closed, so as to form a small retort; and on distilling the fluid four or five times from one angle to the other, all the chlorine may be driven off without any loss of the substance, and it becomes limpid and colourless. It still, however, always contains some perchloride, which has escaped decomposition, and, to separate this, I have boiled the fluid until the tube was nearly full of its vapour, and then closing

the end that still remained open, by a lamp and blow-pipe, have afterwards left the whole to cool. It is then easy by collecting all the fluid into one end of the tube, and introducing that end through a cork into a receiver, under which a very small flame is burning, to distil the whole of the fluid at a temperature very little above that of the atmosphere. The solid chloride being less volatile does not rise so soon, and the pure proto-chloride collects at the external end of the tube. To ascertain its purity, a drop may be placed on a glass plate; it will immediately evaporate, and if it contains perchloride, that substance will be left behind; otherwise, no trace will remain on the glass. The presence or absence of free chlorine may be ascertained by dissolving a little of the fluid in alcohol or ether, and testing by nitrate of silver.

The pure proto-chloride of carbon is a highly limpid fluid, and perfectly colourless. Its specific gravity is 1.5526. It is a non-conductor of electricity. I am indebted to Dr. WOLLASTON for the determination of the refractive power of this chloride, and for the approximation to the refractive power given of the perchloride. In the present case it is 1.4875, being very nearly that of camphor. It is not combustible except when held in a flame, as of a spirit lamp, and then it burns with a bright yellow light, much smoke, and fumes of muriatic acid.

It does not become solid at the zero of Fahrenheit's scale. When its temperature is raised under the surface of water to between 160° and 170° , it is converted into vapour, and remains in that state until the temperature is lowered. When heated more highly, as by being passed over red hot rock crystal in a glass tube, a small portion is always decomposed; nearly all the fluid may, however, be condensed again, but

it passes slightly coloured, and the tube and crystal are blackened on the surface by charcoal. I am uncertain whether this decomposition ought not to be attributed rather to the action of the glass at this high temperature than to the heat alone.

It is not soluble in water, but remains at the bottom of it in drops, for many weeks, without any action.

It is soluble in alcohol and ether, and the solutions burn with a greenish flame, evolving fumes of muriatic acid.

It is soluble in the volatile and fixed oils. The volatile oils containing it burn with the emission of fumes of muriatic acid. When the solutions of it in the fixed oils are heated, they do not blacken or evolve fumes of muriatic acid. It is therefore probable, that when this happens with the solution of the perchloride in fixed oils, it is from its conversion by the heat into proto-chloride and the liberation of chlorine.

It is not soluble in alkaline solutions, nor do they act on it in some days. Neither is it at all soluble in, or affected by, strong nitric, muriatic, or sulphuric acids.

Solutions of silver do not act on it.

Oxygen decomposes it at high temperatures, forming carbonic oxide, or acid, and liberating chlorine.

Chlorine dissolves in it in considerable quantity, but has no farther action, or only a very slow one in common day light; on exposure to solar light, a different result takes place. I have only had two days, and those in the middle of November, on which I could expose the proto-chloride of carbon in atmospheres of chlorine to solar light; and hence the conversion of the whole of the proto-chloride was not perfect; but at the end of those two days the retorts containing the

substances were lined with crystals, which, on examination under the microscope, proved to be quadrangular plates, resembling those of the perchloride of carbon. There were also some rhomboidal crystals here and there. After the formation of these crystals, there was considerable absorption in the retort; hence chlorine had combined; and the gas which remained was chlorine unmixed with any thing else, except a slight impurity. The solid body, on examination, was found to be volatile, soluble in alcohol, precipitable by water, and had the smell and other properties of perchloride of carbon. Hence, though heat in separating chlorine from the perchloride of carbon produces its decomposition, light occasions its reproduction.

It dissolves iodine very readily, and forms a brilliant red solution, similar in colour to that made by putting iodine into sulphuret of carbon, or chloric ether. It does not exert any farther action on iodine at common temperatures.

An electric spark passed through a mixture of the vapour of the chloride with hydrogen, does not cause any detonation, but when a number are passed, the decomposition is gradually effected, and muriatic acid is formed. When hydrogen and the vapour of the proto-chloride are passed through a red hot tube, there is a complete decomposition effected, muriatic acid gas being formed, and charcoal deposited. The mixed vapour and gas burn with flame as they arrive in the hot part of the tube. The vapour of the proto-chloride detonates readily by the electric spark with a mixture of oxygen and hydrogen gases, and a complete decomposition is effected. It will not detonate with the vapour of water.

Sulphur and phosphorus both dissolve in it, but exert no

decomposing action at temperatures at, or below, the boiling point of the chloride. The hot solution of sulphur becomes a solid crystalline mass by cooling. Phosphorus decomposes it at a red heat.

Its action on metals is very similar to that of the perchloride. When passed over them at a red heat, it forms chlorides, and liberates charcoal. Potassium does not act on it immediately at common temperatures; but, when heated in its vapour, burns brilliantly, and deposits charcoal.

When passed over heated metallic oxides, chlorides of the metals are formed, and carbonic oxide, or carbonic acid, according to the state of oxidation of the metal. When its vapour is transmitted over heated lime, baryta, or strontia, the same brilliant combustion is produced as with the perchloride.

Whilst engaged in analysing this chloride of carbon, for the purpose of ascertaining the proportions of its elements, I endeavoured, at first, to find how much chlorine was liberated from a certain weight of perchloride during its conversion into proto-chloride, and for this purpose distilled the perchloride, through red hot tubes into solution of nitrate of silver, receiving the gas into tubes filled with and immersed in the same solution; but I could never get accurate results in this way, from the difficulty of producing a complete decomposition, and also from the formation of chloric acid. 5 grains of perchloride distilled in this manner gave 4.3 grains of chloride of silver, which are equivalent to 1.06 grains of chlorine; but some of the chloride evidently passed undecomposed, and crystallized in the tube.

2.7 grains of the pure proto-chloride were passed over red

hot pure baryta in a glass tube : a very brilliant combustion with flame took place, chloride of barium and carbonic acid were produced, and a little charcoal deposited. When the tube was cold, the barytes was dissolved in nitric acid, and the chlorine precipitated by nitrate of silver. 9.4 grains of dry chloride of silver were obtained = 2.32 grains of chlorine.

Other experiments were made with lime, which gave results very near to this, the quantity of chloride being rather less.

3 grains of pure proto-chloride were passed over peroxide of copper heated red hot in an iron tube, and the gas received over mercury. 3.5 cubic inches of carbonic acid gas came over mixed with .1 of a cubic inch of common air. These 3.5 cubic inches are nearly equal to .449 of a grain of carbon.

These experiments indicate the composition of the fluid chloride of carbon to be 1 proportion of chlorine and 1 of carbon, or 33.5 of the former and 5.7 of the latter. The difference between these theoretical numbers, and the results of the experiments, is not too great to have arisen from errors in working on such small quantities of the substance.

A mixture of equal volumes of oxygen and hydrogen was made, and 2 volumes of it detonated with the vapour of the proto-chloride in excess over mercury by the electric spark. The expansion was very nearly to 4 volumes ; of these, 2 were muriatic acid, and the rest pure carbonic oxide : and calomel had been formed, its presence being ascertained by potash. Hence it appears, that 1 volume of hydrogen and half a volume of oxygen had decomposed 1 proportion of the proto-chloride, forming the two volumes of muriatic

acid gas and 1 volume of carbonic oxide; and that at the intense temperature produced within the tube by the inflammation, the rest of the oxygen and the mercury had decomposed a farther portion of the substance, giving rise to the second volume of the carbonic oxide, and to the calomel.

A mixture of 2 volumes of hydrogen and 1 volume of oxygen was made, and 3 volumes of it detonated with the vapour, as before. After cooling, the expansion was to 6 volumes; 4 of which were muriatic acid, and 2 carbonic oxide. There was no action on the mercury in this experiment. Again, 5 volumes of the same mixture being detonated with the vapour of the substance, expanded to 9.75 volumes, of which 6.25 were absorbed by water, and were muriatic acid, and 3.5 were carbonic oxide mixed with a very small portion of air introduced along with the fluid chloride. These experiments, I think, establish the composition of the proto-chloride of carbon, and prove that it contains 1 proportion of each of its elements.

From a consideration of the proportions of these two chlorides of carbon, it seems extremely probable that another may exist, composed of 2 proportions of chlorine combined with 1 of carbon. I have searched assiduously for such a compound, but am undecided respecting its production. When the fluid proto-chloride was exposed with chlorine to solar light, crystals were formed, as before described. The greater number of these were certainly the perchloride first mentioned in this paper: but when the retort was examined by a microscope, some rhomboidal crystals were observed here and there among those of the usual dendritic and square forms.

These may, perhaps, be the real perchloride; but I had not time, before the season of bright sunshine passed away, to examine minutely what happens in these circumstances; and must defer this, with many other points, till the next year brings more favourable weather.

Compound of Iodine, Carbon, and Hydrogen.

The analogy which exists between chlorine and iodine, naturally suggested the possible existence of an iodide of carbon, and the means which had succeeded with the one element, offered the best promise of success with the other.

Iodine and olefiant gas were put in various proportions into retorts, and exposed to the sun's rays. After a while, colourless crystals formed in the vessels, and a partial vacuum was produced. The gas in the vessels being then examined, was found to contain no hydriodic acid, but only pure olefiant gas. Hence, the effect had been simply to produce a compound of the iodine with the olefiant gas.

The new body formed was obtained pure by introducing a solution of potash into the retort, which dissolved all the free iodine; the substance was then collected together and dried. It is a solid white crystalline body, having a sweet taste and aromatic smell. It sinks readily in sulphuric acid of specific gravity 1.85. It is friable: is not a conductor of electricity. When heated, it first fuses, and then sublimes without any change. Its vapour condenses into crystals, which are either prismatic, or in plates. On becoming solid after fusion, it also crystallizes in needles. The crystals are transparent. When highly heated it is decomposed, and iodine evolved. It is not readily combustible; but when

held in the flame of a spirit lamp, burns, diminishing the flame, and giving off abundance of iodine, and some fumes of hydriodic acid. It is insoluble in water, or in acid and alkaline solutions. It is soluble in alcohol and ether, and may be obtained in crystals from these solutions. The alcoholic solution is of a very sweet taste, but leaves a peculiarly sharp biting sensation on the tongue.

Sulphuric acid does not dissolve it. When heated in the acid to between 300° and 400° , the compound is decomposed, apparently by the heat alone; and iodine and a gas, probably olefiant gas, are liberated. Solution of potash acts on it very slowly, even at the boiling point, but does gradually decompose it.

This substance is evidently analogous to the compound of olefiant gas and chlorine, and remarkably resembles it in the sweetness of its taste, though it differs from it in form, &c. It will with that body form a new class of compounds, and they will require names to distinguish them. The term chloric ether, applied to the compound of olefiant gas and chlorine, did not at any time convey a very definite idea, and the analogous name of iodic ether, would evidently be very improper for a solid crystalline body heavier than sulphuric acid. Mr. BRANDE has suggested the names of hydriodide of carbon, and hydrochloride of carbon, for these two bodies. Perhaps as their general properties range with those of the combustibles, whilst the specific nature of the compound is decided by the supporter of combustion which is in combination, the terms of hydro-carburet of chlorine, and hydro-carburet of iodine, may be considered as appropriate for them.

As yet I have not succeeded in procuring an iodide of carbon, but I intend to pursue these experiments in a brighter season of the year, and expect to obtain this compound.

ON A
NEW COMPOUND OF CHLORINE AND CARBON.

BY

RICHARD PHILLIPS, F.R.S.E. F.L.S. M.G.S. &c.

AND

MICHAEL FARADAY,

CHEMICAL ASSISTANT IN THE ROYAL INSTITUTION.

FROM THE

PHILOSOPHICAL TRANSACTIONS.

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1821.

NEW COMPOUND OF CHLORINE AND CARBON

Gentlemen who are indulged with separate Copies of their Communications, are requested to use their endeavour to prevent them from being reprinted, till one month after the publication of that part of the Philosophical Transactions in which they are inserted.

By Order of the President and Council,

W. T. BRANDE, Sec. R. S.

PHILOSOPHICAL TRANSACTIONS

LONDON

PRINTED BY W. BOURNE AND S. KING, STATIONERS

1821

ON A

NEW COMPOUND OF CHLORINE AND CARBON.

Read before the ROYAL SOCIETY, July 12, 1821.

M. JULIN, of Abo, in Finland, is proprietor of a manufactory in which nitric acid is prepared, by distilling calcined sulphate of iron with crude nitre in iron retorts, and collecting the products in receivers connected by glass tubes, in the manner of **Woulfe's** apparatus. In this process he observed, that when a peculiar kind of calcined vitriol, obtained from the waters of the mine of Fahlun, and containing a small portion of pyrites, known in Sweden by the name of calcined aquafortis vitriol No. 3, was used, the first tube was lined with sulphur, and the second with fine white feathery crystals. These were in very small quantity, amounting only to a few grains from each distillation; but **M. JULIN**, by degrees, collected a portion of it, and, having brought it to this country, inserted a short account of its properties in the *Annals of Philosophy*, Vol. i. p. 216, to which a few observations were added by ourselves.

The following are the properties of this substance, as described by **M. JULIN**. It is white; consists of small soft adhesive fibres; sinks slowly in water; is insoluble in it whether

hot or cold; is tasteless; has a peculiar smell, somewhat resembling spermaceti; is not acted on by sulphuric, muriatic, or nitric acid, except that the latter by boiling on it gives traces of sulphuric acid; boiled with caustic potash, has a small portion of sulphur dissolved from it; dissolves in hot oil of turpentine, but most of it crystallizes in needles from the solution on cooling; dissolves in boiling alcohol of .816, but by far the greater part crystallizes on cooling; burns in the flame of a lamp with a greenish blue flame, giving a slight smell of chlorine gas; when heated, melting, boiling and subliming at a temperature between 350° and 400° , and subliming slowly without melting at a heat of about 250° , forming long needles. Potassium burned with a vivid flame in its vapour in an open tube, and carbon was deposited; a solution made of the residuum, and saturated with nitric acid, gave a copious precipitate with nitrate of silver. M. JULIN then remarks, that the small quantity he possessed, with want of leisure, prevented him from making any farther experiments on it; and concludes, by comparing it with the chlorides of carbon that have lately been formed.

The small quantity of the substance which, by the kindness of M. JULIN, we had at our disposal at that time, was insufficient to enable us satisfactorily to ascertain its nature. We found it mixed with free sulphur, and sulphate and muriate of ammonia. When purified, our first object, in consequence of M. JULIN's suggestion, was to compare it with the per-chloride of carbon, but it was found entirely distinct from it in its properties.

Since M. JULIN's return from the continent, he has very kindly placed some farther portions of this substance at our

disposal. We have therefore been enabled to continue our experiments, and have come to the very unexpected conclusion of its being another chloride of carbon, in addition to the two, an account of which has been published in the Transactions of the Royal Society for this year.

The substance, after being boiled in solution of potash, washed in water, dried and sublimed, formed beautiful acicular crystals, which appeared to Mr. W. PHILLIPS to be four-sided prisms. They contained no sulphur, and, when dissolved in alcohol or ether, gave no traces of chlorine or muriates, by nitrate of silver. They burned in the air with a strong bright flame at a heat below redness, and agreed with the description given by M. JULIN of the properties of the substance.

When heated moderately, it sublimed unaltered; but on passing a portion over rock crystal, heated to bright redness, in a green glass tube, it was decomposed, charcoal was deposited, and the gas, passed into solution of nitrate of silver, precipitated it, and proved to be chlorine.

A portion was repeatedly sublimed in a small retort filled with chlorine, which was made red hot in several places; it however underwent no change; but on cooling crystallized as at first. It was also exposed in the same gas to sun light for many days, but no change took place.

When raised in vapour over hot mercury, and detonated with excess of oxygen, a quantity of carbonic acid gas and chloride of mercury were produced. There was no change in the volume of gas used; and lime water being passed into it, absorbed the carbonic gas, became turbid, and left a residuum of pure oxygen. Acetic acid being then added, to dissolve the carbonate of lime, the solution was tested for

chlorine, which was readily found in it. When detonated with oxygen, the substance being in excess, there was expansion of volume, carbonic oxide, carbonic acid, and chloride of mercury being formed.

When phosphorus, iron, tin, &c. were heated to redness in its vapour over mercury, it was decomposed, chlorides of those substances being formed, and charcoal deposited; and M. JULIN has shown that the same effect is produced by potassium.

Three grains of this substance were passed in vapour over pure peroxide of copper, heated to redness in a green glass tube: a very small portion passed undecomposed. The gas received over mercury equalled 5.7 cubic inches; it was carbonic acid gas. A small part of the oxide of copper was reduced, and portions of a crystalline body appeared within the tube, which, on examination, proved to be chloride of copper. Some of this was used in making experiments on its nature; but when that was ascertained, the remaining contents of the tube were dissolved in nitric acid, and precipitated by nitrate of silver: 6.1 grains of chloride of silver were obtained.

Two grains were passed over pure quick lime, raised to a red heat in a green glass tube. The moment the vapour came in contact with the hot lime, ignition took place, and the earth burned as long as the vapour passed over it. When cold, the tube was examined, and much charcoal found deposited at the spot where the ignition occurred. The contents of the tube were dissolved in nitric acid, and the filtered solution precipitated by nitrate of silver: 5.9 grains of chloride of silver were obtained.

These results afford us sufficient data from which to deduce the nature and composition of this body. All the experiments of decomposition indicate it to contain chlorine and carbon, and those with oxygen and the metals, sufficiently prove the absence of hydrogen and oxygen. With regard to the proportions of the elements, three grains of the substance gave 5.7 cubic inches of carbonic acid gas, therefore two grains will give 3.8 cubic inches. One hundred cubic inches of carbonic acid gas weigh 46.47 grains, and contain 12.72 grains of carbon; and 3.8 cubic inches will therefore contain 0.483 grains of carbon. The two grains of the substance decomposed by heated lime gave 5.9 grains of chloride of silver, which, according to Dr. WOLLASTON'S scale, equal 1.45 of chlorine; hence the two grains gave chlorine - - - 1.45

carbon - - - .483
 1.933

The loss here is 0.067, which is by no means important, when the small quantity of the substance and the nature of the experiments are considered.

As to the proportion of these two bodies to each other, if we consider chlorine as represented by 33.5, and carbon by 5.7, or with Dr. WOLLASTON by 44.1 and 7.5, then the 1.45 of chlorine would be equivalent to 0.2466 of carbon. This is the constitution of the fluid or proto-chloride of carbon; and if we double the 0.2466, the product 0.4932, approaches so near to the experimental result 0.483, that we do not hesitate to regard this compound as consisting of one portion of chlorine and two portions of carbon, or

chlorine - - - 44.1 - - - 33.5
 carbon - - - 15 - - - 11.4

It is remarkable, that another of these compounds should be found so soon after the discovery of the two former chlorides of carbon. Its physical properties, and its chemical energies, are in every respect analogous to those of the former compounds; and its constitution increases the probability, that another chloride of carbon may be found, consisting of two portions of chlorine and one of carbon.

All the endeavours we have yet made to form the chloride of carbon now described, or to convert it into either of the other chlorides, have been unsuccessful. We expected that when decomposed by heat, it would produce the protochloride with the liberation of carbon, as the perchloride does with the liberation of chlorine, but we have not yet been able to ascertain that point. We have only to offer as an apology for this and other imperfections in the present paper, the smallness of the quantity of this substance that we possessed.