Chlorine — an introduction

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Abstract: Chlorine, in the form of its salts, has been known since the earliest days of recorded history, although its recognition as an element did not occur until the beginning of the nineteenth century when its very high reactivity as an oxidant was found remarkable after it was shown not to contain any oxygen. Its absorption by sunlight made it a key substance in the early development of photochemistry. One example of this, with both pure and applied aspects, is described in more detail. The free radical chloric oxide played an important role in the development of the technique of flash photolysis and twenty five years later these researches were of essential importance in showing how chlorine and its oxides were involved in the destruction of the ozone layer by the chlorofluorocarbons.

INTRODUCTION

The best known of all chemical substances must be 'common' salt, or its solution in water called brine, both of which have been known and used from the earliest times. In fact we and other living creatures evolved and made their first homes in a solution of brine. One of the earliest of the livery companies, or guilds, of London was the company of Salters, founded six hundred years ago which still today is the company most closely affiliated to chemistry and the British chemical industry. The high place of salt in man's history is marked in many ways : if we are good we are 'the salt of the earth' and our inferiors at the table sit 'below the salt.' If they are 'not worth their salt' they may lose their 'salary' which was often paid in salt.

Salt is not only common and abundant, it is one of the most stable of chemical substances. And yet it is made of two of the most reactive elements commonly encountered by chemists - sodium and chlorine. Their high reactivity, especially with each other, is due to the fact that, apart from the inert gases, they are respectively members of the first and last groups of the periodic table. The inert gases are inert because they have a stable outer octet (or pair) of electrons and the other elements forever strive to attain this restful state.

Sodium and the other elements in the first group have one electron more than the octet and try to give it up. Chlorine and the other halogens in group 7 are short of one electron to complete the octet and strive to steal one from the elements around them. If they achieve this objective they become charged 'ions,' sodium ions being minus an electron and therefore positive and chlorine ions being plus an electron and negative. The ions, having complete outer shells, are stable, like the inert gases, and so it comes about that the salt, sodium chloride, formed from these two violently reactive and poisonous elements is not only safe to eat, it is essential to life. And the element chlorine, seeking another electron wherever it can be found and being, therefore, a strong oxidising agent like oxygen itself, is a destroyer of life and a useful bactericide.

EARLY HISTORY

Chlorine was discovered by Scheele in 1774 but was not known as an element. Because of its strong oxidising properties it was thought by most chemists, including Lavoisier, to contain oxygen and was called oxymuriatic acid (muriatic acid being HCl). It was Humphry Davy, working at the Royal Institution in London in early nineteenth century, who showed that the gas did not react with red hot carbon and contained no oxygen, declared that it was an element and named it chlorine after its colour.

Davy also prepared sodium and other alkali metals and showed that they too were elements. As a result of this important work he was invited to Paris to receive a medal from Napoleon and was welcomed with the greatest hospitality at the height of the wars between their two countries. Whilst he was there he studied another halogen, iodine, discovered by M.Courtois, a saltpetre manufacturer in Paris. In 1812, Davy, who was given a sample by Ampere, showed that it was an element like chlorine. In 1813 he also prepared the lightest halogen, fluorine, in a mixture with hydrogen fluoride. The other common halogen, bromine was discovered in 1826 by a chemist named Ballard, from the Ecole Normale, who was otherwise so little known that it was said, rather ungraciously, that Ballard was discovered by Bromine.

Davy was accompanied on this journey by Michael Faraday, his young assistant and chlorine played a key part in this association of the two great chemists. Davy was oblivious to danger, either to himself or to his assistant, and he happily prepared the vicious compounds of chlorine, ClO_2 and NCl_3. It was when he was nearly blinded in one of these experiments that he called in Faraday to help. It was Faraday who later, at Davy's suggestion, heated chlorine hydrate in a closed glass tube and prepared liquid chlorine - this was the first liquefaction of any 'permanent' gas. The event was described by Faraday's biographer, Paris, as follows:

'Upon descending into the laboratory at the Royal Institution (March 1823) I found Mr Faraday engaged in experiments on chlorine and its hydrate in closed tubes. It appeared to me that the tube in which he was operating...contained some oily matter and railed him on the carelessness of employing soiled vessels. Mr Faraday, on examining the tube, acknowledged the justness of my remark and expressed his surprise at the circumstance...he immediately proceeded to file off the sealed end when, to our great astonishment, the contents suddenly exploded and the oily matter vanished. Early the next morning, I received from Mr Faraday the following laconic note
'Dear Sir, The oil you noticed yesterday turns out to be liquid chlorine'
Yours faithfully, M. Faraday.

Chlorine was, not surprisingly perhaps after these excitements, the subject of one of the first lectures delivered by Faraday to the City Phil Society in 1816. He concluded as follows: 'Before leaving this substance chlorine, I will point out its history as an answer to those who are in the habit of saying of every new fact "what is its use?" Dr Franklin says to such 'what is the use of an infant?' When Scheele discovered this substance it appeared to have no use, it was in its infantine and useless state; but, having grown up to maturity, witness its powers and see what endeavours to make it useful have done.'

CHLORINE THE PHOTOCHEMISTS ELEMENT

Chlorine, being a greenish yellow gas, absorbs visible light and is therefore a convenient element for photochemical study, indeed it has played a key role in the development of chemical kinetics as well as photochemistry. The photochlorination of organic compounds, again pioneered by Davy and Faraday, was used as a preparative method in the early nineteenth century especially to make that most important class of solvents, the chlorinated hydrocarbons. Faraday's first important discoveries as a chemist were the two chlorides of carbon—C_2Cl_6 and C_2Cl_4 and hexachlorobenzene C_6Cl_6.

The explosive combustion of mixtures of chlorine and hydrogen were spectacular evidence of the power of chemical combination and led to the recognition of the existence of free atoms and, a little later to the idea of chain reactions introduced by Nernst. Following Planck's quantum theory, the law of photochemical equivalence of Stark and Einstein had led to a belief, probably not intended, that one quantum of light results in the reaction of one molecule. This is, of course, very rarely the case and most clearly not so in the reaction of chlorine and hydrogen.

Quantum yield measurements soon established that one quantum of light, absorbed (in accordance with the Einstein law) by one molecule of chlorine, results ultimately in the dissociation of as many as a million molecules of chlorine. The two atoms of chlorine formed in the initial photochemical act react with two molecules of hydrogen to form two molecules of hydrogen chloride and two atoms of hydrogen which then react with two further molecules of chlorine and so propagate the chain. Nernst's theory of this and other chemical chain reactions was established long before the nuclear chain reactions, which operate on similar principles, provided their even more spectacular explosions.

For many years the evidence for free atoms, free radicals and their reactions was indirect until, in 1949, in our laboratory in Cambridge, it became possible to observe directly their formation, their spectra and

their reactions. Not surprisingly, chorine gas was one of the first substances that we studied. Our technique of flash photolysis was very simple in principle: a brief flash of light, a few thousandths or millionths of a second in duration, was used to irradiate the substance of interest and, a brief interval later, a second flash of light recorded the products of reaction.

When chlorine gas is irradiated in the normal way with a continuous light source there is no chemical change although it has long been known that there is an increase in pressure in the closed vessel when the energy of the light absorbed by the chlorine is released as heat in what is known as the Budde effect. In our flash photolysis experiment however, we observed a bleaching of most of the chlorine which we interpreted as the conversion of chlorine molecules into atoms .The atoms do not absorb light in the visible and ultra violet regions. The bleaching lasted several milliseconds because two chlorine atoms cannot combine directly; they will dissociate again unless they get rid of the energy of recombination. That this requires the presence of a third body, or chaperone, had been predicted for many years but now it was possible to observe the chaperone effect and measure its effect in chlorine atom recombinations.

Chlorine also played an important role in our next experiments which recorded the first free radical absorption spectra and time resolved studies of free radical reactions. The first free radical absorption spectrum to be observed was a new compound of chlorine and oxygen. I would like to describe these results as examples of the very interesting photochemistry of chlorine oxides and the part these reactions play in the photochemistry of the atmosphere and stratosphere.

CHLORIC OXIDE

In the course of the experiments on the flash photolysis of chlorine some oxygen was admitted to the vessel and a splendid new band spectrum appeared, with a lifetime of a few milliseconds. It was soon shown to be a diatomic molecule hitherto unobserved, the free radical ClO or chloric oxide. [1]
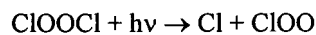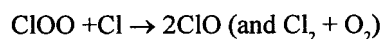
The ClO was formed by the reactions [2]:

$$Cl_2 + h\nu \rightarrow 2Cl \tag{1}$$

$$2Cl + O_2 \rightarrow 2ClO \tag{2}$$

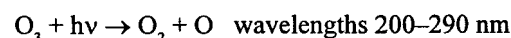and reversed by the dark reaction

$$2ClO \rightarrow Cl_2 + O_2. \tag{3}$$

Further study showed [3] that there were intermediate steps as follows

$$Cl + O_2 (+ M) \leftrightarrow ClOO (+ M) \tag{4}$$

$$ClOO + Cl \rightarrow 2ClO \text{ (and } Cl_2 + O_2)$$

$$2ClO \rightarrow ClOOCl \rightarrow Cl_2 + O_2$$

$$ClOOCl + h\nu \rightarrow Cl + ClOO$$

but since there was no overall final change these details seemed to be of little importance. It was some twenty-five years later that this work, like most 'useless' fundamental research, became essential to understanding the role of chlorine on the ozone of the stratosphere.

CHLORINE IN THE ATMOSPHERE

The mechanism of the photochemical formation the stratospheric ozone layer was explained by Sidney Chapman in 1930 in terms of the reactions:

$$O_2 + h\nu \rightarrow 2O \quad \text{wavelengths below 230 nm}$$

$$O + O_2 \rightarrow O_3$$

$$O_3 + h\nu \rightarrow O_2 + O \quad \text{wavelengths 200–290 nm}$$
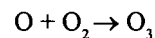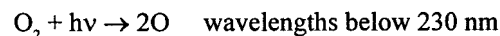
Clearly if there was any chlorine in the stratosphere it would upset this steady state by adding the reactions:

$$Cl + O_3 \rightarrow ClO + O_2$$
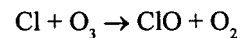
However, no sources of chlorine in the stratosphere were known so that, although the reactions of ClO continued to be of interest to photochemists through the sixties, they seemed to have little relevance to the ozone layer, or to anything else for that matter.

In 1971 James Lovelock, working mainly at home in Britain, found that traces of chlorofluorocarbons or CFC's, used as aerosol propellants and refrigerants, had pervaded the entire troposphere [4]. But Lovelock saw no cause for alarm in this, being so inert seemed to make the CFCs harmless.

Fortunately another scientist, Professor F. Sherwood (Sherry) Rowland, in the Chemistry Department of the University of California at Irvine began to wonder where, if they were so stable, the CFCs would eventually go. With a photochemist who had joined him from Mexico City, Dr. Mario Molina, he set out in 1973 to study the life story of CFCs.[5]

As photochemists, they knew that even stable CFCs would be broken down by light but that they only absorbed light in the far ultraviolet region. This not only means that if they reach the stratosphere they will be destroyed, probably forming chlorine and destroying the ozone layer, but what is more they will reach the ozone layer because they will not be destroyed in the troposphere, by near ultra-violet light, as most other organic substances are. In fact Rowland and Molina estimated that CFCs would have lifetimes of between forty and one hundred and fifty years before being decomposed in the stratosphere. Once that happens, each atom of chlorine could destroy, through its chain reactions, as many as a hundred thousand molecules of ozone.

But people were not impressed by theories and experimental studies of total ozone had shown no convincing change.

Convincing evidence now came however from a totally unexpected source—the Antarctic survey. In 1953 the Royal Society had sent an expedition to Antarctica, and the advance party established a base there in 1955 which it named 'The Royal Society Base, Haley Bay.' Observations on the ozone column began in the late 50's and have continued ever since. The measurements were almost constant into the 1970s and then a decline began in the October ozone values. In 1985, J.C. Farman of the British Antarctic Survey reported a seasonal reduction of ozone over Haley Bay [6], and in 1987 comprehensive measurements showed that the springtime depletion of ozone over Antarctica was quite spectacular and occurring elsewhere could have been catastrophic since 95% of the ozone between the altitudes of 14 and 23 km was destroyed in less than two months. This was a total surprise and a grave warning, though it was still unproven that the culprits were CFCs.

But that evidence was soon to come, results as convincing as we are ever likely to be blessed with. The free radical, ClO, appeared rapidly and abundantly in the late August and this was followed by a dramatic fall in ozone in mid-September, which showed an inverse correlation even in the smallest details. All other gases such as the nitrogen oxides and even water H_2O, decreased with ozone, only ClO increased. Intermediates such as ClOOCl reactions 6 and 7 and the low temperature surface reactions accounted for the seasonal variations. The 'smoking gun' had at last been found and all the fingerprints were in place.

The result of these discoveries, as well as others in the northern hemisphere, has been almost universal acceptance of the implication of CFCs in the destruction of ozone and a surprisingly rapid and successful international activity. In September 1987 the Montreal protocol, signed by 24 countries, agreed that consumption of CFC 11 and 12 should be frozen at 1986 levels in 1989, reduced by 20% in 1993/4 and to 50% of 1986 levels by 1998/9.

The ozone conferences in London in March 1990, attended by 123 countries, and in Helsinki in May, took matters further, with the agreement of more nations, including a number of important developing countries.

The story is by no means ended, scientific understanding is still far from complete, and there is still strong resistance from the manufacturers and user of CFC's in some countries. But we now know that there is a real problem and we know that, given the will, it can be solved.

The moral of this story is that we must not use the power of the knowledge that we now possess to manipulate the world, without ensuring that we also have the knowledge to understand and mitigate unforeseen errors or disasters.

There has been much pressure in recent years to concentrate our scientific efforts on the applications at the expense of fundamentals. But there is no way that humans can foresee all the consequences of their actions, no way that a committee can plan a safety programme or a disaster programme that will always work. The only sure foundation for security in this technological world is to have a science base which is

continually asking whatever questions seem interesting and is always there to advise and to act when the need arises. The unforeseen consequences of the otherwise safe and excellent CFC's cannot be blamed on the industrial chemists or their managers who did all reasonable testing that was expected of them. But it was left to the individuals freely following hunches which were in the first place totally unconnected with the ozone layer, the early photochemists and atmospheric chemists, then Lovelock, and Rowland and Farman to say things that had never been said or thought before. It was they who saved us from what might have been disaster.

It is unsafe to build a complex technological world, available to ten billion human beings, without a world base of scientific understanding which has strong branches in each country that participates in technology. We shall come to no great harm if we go a little more slowly in applying our science and give a higher priority to getting a better understanding of the world where it is to be applied and of the people who apply it. This understanding is particularly important for the young; if they are shielded too closely from the properties and behaviour of potentially dangerous substances like chlorine; if such substances can only be explored in the presence of safety 'officers', then children will not only be excluded from a personal experience of real chemistry, and miss much of the beauty and the excitement of the natural world, but they will be unprepared for the hazards that will inevitably be encountered in later life.

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