

**CXL. Contributions to the Knowledge of Conjugate Compounds.** By Dr. H. KOLBE, Chemical Assistant in the University of Marburg.

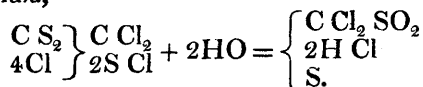
THE examination of the products arising from the decomposition of sulphuret of carbon by means of chlorine has led to the discovery of an interesting series of bodies, which belong, almost without exception, to the class of the so-called conjugate compounds\*, and among them the substitution of chlorine by hydrogen is particularly observed, which will probably throw considerable light on the constitution of certain organic combinations. These compounds, produced almost by the direct combination of their elements, have such a strong similarity to those considered to belong to organic chemistry, that it is impossible here to draw a distinct line between organic and inorganic bodies.

I have already † shown that chlorine and sulphuret of carbon carefully dried are decomposed into a mixture of chloride of sulphur and perchloride of carbon; this takes place not merely at a red heat but at ordinary temperatures, in daylight as well as in the dark. This perchloride of carbon is identical with Regnault's "*ether chlorhydrique de l'esprit de bois perchlorure*," and may be obtained with ease from the chloride of carbon. Perchloride of carbon does not enter into direct combinations, but it unites with sulphurous acid when both are in a nascent state, and forms conjugate, neutral, indifferent bodies, which Berzelius and Marcet discovered when they

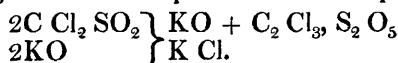
\* "*Corps copulés*" of Gerhardt.

† Liebig's *Annal.* Bd. xlv. p. 41.

digested sulphuret of carbon with moistened chlorine or nitric acid\*. I call this white, volatile, crystallized compound sulphite of perchloride of carbon,  $C Cl_2 SO_2$ . It may be obtained in large quantities by digesting peroxide of manganese and hydrochloric acid for several days in a close vessel with sulphuret of carbon, and after the decomposition is complete distilling the mixture. Its formation is explained by the following formula,—



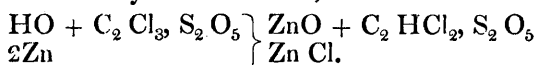
Sulphite of perchloride of carbon suspended in water is reduced by chloride of tin, sulphuretted hydrogen, or sulphurous acid, and converted with the loss of one equivalent of chlorine into sulphite of chloride of carbon,  $C Cl SO_2$ , a colourless, inodorous, and very unstable combination, soluble in water and alcohol. The solution in water is decomposed upon exposure to the air, combining with one equivalent of oxygen, forming oxide of chloride of carbon and sulphurous acid. Chlorine occasions a precipitate of regenerated sulphite of perchloride of carbon. Bromine also produces a similar insoluble combination, which will be the subject of a future examination. Iodine occasions no precipitate. The behaviour of sulphite of perchloride of carbon towards the caustic alkalis gives rise to a series of conjugate hyposulphates, which have the greatest similarity to one another, although their conjunctives, by which they are alone distinguished, are bodies of quite a different chemical nature. The acids thus produced do not show the slightest similarity to sulphurous acid; the chemical properties of the latter are upon formation of the conjoined bodies completely changed, and they have obtained properties and a power of combination which place them by the side of the strongest inorganic acids. The first of these combinations is hyposulphate of chloride of carbon,  $HO + C_2 Cl_3, S_2 O_5$ . It contains as a conjunct perchloride of carbon, and is formed together with chloride of potassium when the sulphite of perchloride of carbon is dissolved in caustic potash. The potash salt crystallizes after evaporation of the neutral solution in large rhombic tables, which effloresce upon exposure to the air. The crystals contain one atom of water; the effloresced salt is free from water, and is composed of  $KO + C_2 Cl_3, S_2 O_5$ . This decomposition is thus explained—



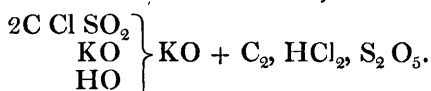
\* Berzelius's Chemistry, i. p. 622.

The hydrous hyposulphate of chloride of carbon, which is obtained by precipitation of the baryta salt with sulphuric acid, crystallizes upon evaporation in small prisms, not permanent in the air, which may be heated to  $150^{\circ}$  without decomposition. They are not oxidated by boiling with nitric, nitromuriatic or chromic acids; nitric and hydrochloric acid may be distilled off from it without any change. The salts of hyposulphate of chloride of carbon are soluble in water and in alcohol, and easily crystallizable. They are decomposed by heat into sulphurous acid, chloro-carbonic oxide gas, and the metallic chloride, which last remains free from sulphuric acid, and is colourless. The barytic salt is formed like the alkaline salt, by solution of the sulphurous perchloride of carbon in baryta water; it crystallizes upon evaporation in large four-sided tables; at  $100^{\circ}$  Cent. it is composed of  $\text{BaO} + \text{C}_2\text{Cl}_3, \text{S}_2\text{O}_5 + \text{aq.}$  The remaining salts are formed by neutralising the free acid with a basic carbonate. The ammoniacal salt crystallizes most readily in fine large prisms.

Hyposulphate of chloride of formyl,  $\text{HO} + \text{C}_2\text{HCl}_2, \text{S}_2\text{O}_5$ , is the second in this class of coupled acids. It is formed by the substitution of one equivalent of hydrogen for one equivalent of chlorine of the hyposulphate of chloride of carbon, when zinc is dissolved by hyposulphate of chloride of carbon, which takes place without the evolution of hydrogen, but with the formation of hydrochloric acid,



The potash salt,  $\text{KO} + \text{C}_2\text{HCl}_2, \text{S}_2\text{O}_5$ , is also obtained by boiling caustic potash with sulphite of chloride of carbon, which combines with one atom of water,

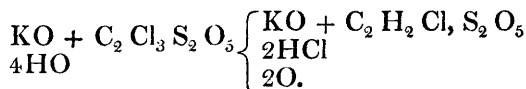


This salt is easily soluble in water and hot alcohol, difficultly soluble in cold alcohol; crystallizes from a hot, saturated alcoholic solution in small, shining nacreous leaves; dried at  $100^{\circ}$  it is anhydrous, and is resolved at  $250^{\circ}$  C. into hydrochloric acid, sulphurous acid, carbonic acid and oxide of carbon; chloride of potassium slightly coloured by charcoal remains behind. The free acid may be obtained by precipitating the alcoholic solution of the potash salt with sulphuric acid. The filtered acid solution may be evaporated, and the excess of sulphuric acid precipitated either by carbonate of lead or baryta water. The hydrate of the hyposulphate of chloride of formyle forms a thick liquid, which crystallizes,

*in vacuo* over sulphuric acid, in small scales, and is similar both in its stability and power of combination to the hyposulphate of chloride of carbon. The silver salt,  $\text{Ag } \ddot{\text{O}} + \text{C}_2 \text{HCl}_2, \text{S}_2 \text{O}_5$ , is very sensitive both to light and heat; it can only be obtained in a crystallized state in a vacuum and in the dark; when dry it will bear a temperature of  $100^\circ \text{C}$ . without change.

Hyposulphate of chlor-elayl,  $\text{HO} + 2\text{C}_2 \text{H}_2 \text{Cl}, \text{S}_2 \text{O}_5$ , contains chloride of elayl as a conjunct, or another isomeric compound. It is formed by the substitution of two equivalents of hydrogen for two equivalents of chlorine of the hyposulphate of chloride of carbon, when a solution of hyposulphate of chloride of carbon and potash is acidified by sulphuric acid, and decomposed by a galvanic current. Two pairs of the Bunsen carbon and zinc series are required for it; two amalgamated zinc plates were the electrodes.

The average power of the current, as measured by Weber's galvanometer, was  $82^\circ$ , equal to a deflection of the needle of  $55^\circ$ . The hydrogen in the nascent state unites with the chlorine of the hyposulphate of chloride of carbon at the cathode, and forms muriatic acid; the equivalents of chlorine are substituted by equivalents of hydrogen. This exchange only proceeds in the formation of the hyposulphate of chlor-elayl, as long as the fluid which is to be decomposed contains an excess of acid,

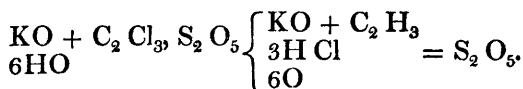


The oxygen is not set free by the above decomposition, but unites with the zinc of the anode; but if the fluid is so far saturated with sulphate of zinc, that the reduced zinc is deposited on the cathode, then it must be precipitated with carbonate of potash, and the filtered fluid being again rendered acid, must be once more exposed to decomposition by the current. This operation is to be repeated as long as traces of chloro-hypsulphate of formyl are perceived, which will be known when the potash salt of the hyposulphate of chlor-elayl, to be extracted out of the fluid precipitated by carbonate of potash and evaporated to dryness, gives out muriatic acid at a red heat. It is impossible to separate both the salts when they appear mixed.

The potash salt of the hyposulphate of chlor-elayl is very much like the salt of hyposulphate of chloro-formyl; it crystallizes out of hot alcohol in small needles, and differs, as before stated, principally by its behaviour at a red heat. It

is precipitated by diluted sulphuric acid and chloride of calcium, which remains of a dark black by the separation of carbon; in fine, the hyposulphate of chlor-elayl is quite like the hyposulphate of chloro-formyl. If a platinum anode be used in the above decomposition of the potash-hyposulphate of chloride of carbon, then the free oxygen acts on the compound and oxidizes it. There goes off at the anode a mixture of chlorine, oxygen and carbonic acid, and after the decomposition is finished there is contained in the fluid only hypochlorate of potash and bisulphate of potash. Under the same conditions the solution of chloride of potassium changes into hypochlorite of potash, and ultimately into chlorate of potash; hypochlorite of potash is only formed in the presence of free acid. Iodide of potassium likewise becomes iodate of potash; I could not produce a *fluorate* of potash from the decomposition of fluoride of potassium.

*Hyposulphate of methyl* =  $\text{HO} + \text{C}_2 \text{H}_3, \text{S}_2 \text{O}_5$ . This compound concludes the series of conjugate hyposulphites. It contains as conjoined a carbo-hydrogen corresponding to the bichloride of carbon, which possesses the same composition as the radical of methyl. It may be produced in the same manner as the above acid, by means of the galvanic current, from hyposulphate of chloride of carbon and potash when the solution contains free alkali. The decomposition takes place as represented by the following formula:—



The uncombined hyposulphate of methyl exhibits also the greatest resemblance to the hyposulphate of chloro-formyl, and is produced like it from the alcoholic solution of the potash salt by precipitating with sulphuric acid. The concentrated acid crystallizes *in vacuo* over sulphuric acid in delicate, easily soluble laminæ, which may be heated to  $130^\circ \text{C}$ . without decomposition. It cannot be oxidized by nitric or by chromic acid, and forms only insoluble crystalline salts.

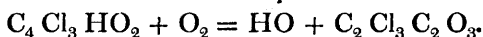
The potash salt,  $\text{KO} + \text{C}_2 \text{H}_3, \text{S}_2 \text{O}_5$ , at  $100^\circ \text{C}$ . is dissolved with difficulty in cold absolute alcohol; and the hot saturated solution crystallizes during the cooling in soft, silky fibres, which form so close a texture, that the mother-water appears gelatinous. On being heated a liquor separates, which has a neutral reaction, and there is also obtained a fetid, volatile product, not further examined: there remains bisulphate of potash mixed with charcoal.

The lead salt,  $\text{PbO} + \text{C}_2 \text{H}_3, \text{S}_2 \text{O}_5 + \text{Aq}$ , crystallizes by

spontaneous evaporation in large prisms: it has a feeble acid reaction, a sweetish taste, and when dried at  $100^{\circ}$  C. is anhydrous. By boiling with oxide of lead a basic salt is produced,  $\text{PbO} + \text{C}_2 \text{H}_3 \text{S}_2 \text{O}_5 + 2\text{PbO}$ , which becomes dull by exposure to the air from the separation of carbonate of lead, and in a vacuum dries up into an amorphous saline mass.

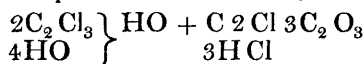
The silver salt,  $\text{AgO} + \text{C}_2 \text{H}_3 \text{S}_2 \text{O}_5$ , admits of evaporation by heat, and only becomes slowly blackened by exposure to the light. It crystallizes in small, thin, anhydrous laminæ, and by a red heat leaves pure metallic silver. All the four conjugate hyposulphates agree further in not uniting with oxide of ethyl to form an æther. In respect to its composition, the hyposulphate of chloro-carbon is ranked with the oxalate of chloro-carbon, or the combination which is known under the name of chlor-acetic acid.

*Oxalate of chloro-carbon*,  $\text{HO} + \text{C}_2 \text{Cl}_3 \text{C}_2 \text{O}_3$ .—As respects the chemical properties of this compound, I have but little to add to the minute investigations of Dumas, as I found that Melsen's statement on the reproduction of acetic acid by means of the potassium amalgam was perfectly corroborated. Respecting its formation, I may mention that it can be also obtained from the oxidation of chloral by fuming nitric acid, or with a mixture of chlorate of potash and muriatic acid,—



Further, chloral is to oxalate of chloro-carbon what aldehyde is to acetic acid. This body, about the constitution of which there have already been so many opinions expressed, is also to be considered as a conjoined compound of formylic acid with perchloride of carbon,  $\text{C}_2 \text{Cl}_3 \text{O}_2 \text{HO}_2$ , an opinion which not only shows the oxidation to form oxalate of chloro-carbon, but also explains simply and sufficiently the origin of aldehyde and the known decomposition into perchloride of formyl and formic acid.

Perchloride of carbon and oxalic acid can unite to form oxalate of chloro-carbon, if they are brought together at the moment of their production. This takes place if chloride of carbon ( $\text{C Cl}$ ) is exposed, under a layer of water, with chlorine to the sunlight. One part of the perchloride of carbon produced is decomposed in the nascent state by water to form muriatic acid and oxalic acid; the latter of which unites with another part of the perchloride of carbon, thus—



The oxalate of chloro-carbon remains dissolved in water, and may be ultimately separated from the muriatic acid mixed

with it and crystallized, by evaporation *in vacuo* over lime and sulphuric acid. The silver salt of this acid does not contain any hydrogen: it detonates by heating, and becomes black by exposure in the air. 0.396 grm. left by a red heat 0.210 grm. chloride of silver.

0.658 grm. burned with oxide of copper, produced 0.214 grm. of carbonic acid. These numbers correspond in 100 parts to 39.9 of silver and 8.9 of carbon. The formula  $\text{Ag O} + \text{C}_2 \text{Cl}_3 \text{C}_2 \text{O}_3$  requires 40.0 silver and 8.9 of carbon.

If we admit these simple facts, then it follows that the acetic acid, which has been until now only known as a product of the oxidation of organic matters, can be also formed synthetically from its elements. Sulphuret of carbon, chloride of carbon, and oxalate of chloro-carbon are the members which in conjunction with the elements of water constitute the means of transition from carbon to acetic acid.

The oxalate of chloro-carbon can also be changed like the hyposulphate of chloro-carbon by the galvanic current, alkali being present, into acetic acid. I have likewise obtained certain signs of the existence of the corresponding members of the hyposulphate of chloro-formyl and hyposulphate of chloro-elalyl, which lie between the oxalate of chloro-carbon and acetic acid. All these facts seem to speak in its favour, and make it at the same time highly probable that the acetic acid is a conjoined compound, or, in other words, methyl-oxalic acid,  $\text{HO} + \text{C}_2 \text{H}_3, \text{C}_2 \text{O}_3$ .

I shall communicate these observations in a future paper after the examination is terminated.

It follows from the above, that without doing homage to the new theory of substitution, we may assume, as an undoubted fact, a reciprocal exchange of hydrogen and chlorine. Methyl or perchloride of carbon may be conjoined with hyposulphuric acid, the character of the compound will be little changed by it; but nevertheless, there is no reason for supposing hyposulphate of methyl to be hyposulphate of chloro-carbon, in which hydrogen takes the part of chlorine. The assertion reversed would be equally true. It is a constant fact that several, perhaps, isomorphic combinations *can* be represented as conjuncts of one and the same acid, without an essential change of the acid properties of the conjoined body. The organic bases containing chlorine, which have been newly discovered by Hofmann, may perhaps be elucidated in a similar point of view.