To sum up, we have been able to analyse the process of phototropic stimulation into the primary electro-physiological perception process which causes the remarkable polar division of sensitiveness between the apex and the base and by this means has become the actual cause of the irreversibility of the phototropic curvature effect and in addition, secondarily, the photochemical process which brings about the curvature. Possibly we may be able to refer the decrease of the phototropic curvature effect by means of greater quantities of energy, as also rectipetality, to the origin of polarisation currents, to which the polar accumulations of ions in their turn give rise.

Utrecht, September 1911.

Chemistry. — *"The photochemical transformations of Ferri-trichloro-acetate solutions"*. By Prof. F. M. JAEGER. (Communicated by Prof. v. ROMBURGH).

(Communicated in the meeting of September 30, 1911).

§ 1. When carrying out some few years ago a series of investigations relating to the photochemical transformations of certain iron-salts by exposure to the light, I noticed that the almost colourless solution, which forms, if freshly precipitated ferric hydroxide is shaken for some days, in the dark, with an excess of an aqueous solution of trichloroacetic acid, — rapidly deposits, when exposed to the light, a white crystalline substance; while, simultaneously, a colourless gas collects in the closed limb of the U-tube employed. Although a more fully detailed article on the many questions which present themselves, will appear shortly, a few preliminary communications are already following here, regarding this remarkable photochemical reaction.

§ 2. Originally the solutions were prepared by shaking freshly precipitated ferric hydroxide, after prolonged and complete washing, in stoppered bottles with an aqueous solution of thrichloroacetic acid for some days in the dark. The *colourless* solution may be kept unaltered in the dark for an indefinite time; but when exposed to daylight, it splits off, after some time, a white crystalline substance with a peculiar odour. If an *excess* of Fe_2O_3 is taken, the solution obtained is *orange-yellow*; it is then *not* sensitive to light, but it regains this property as soon as the solution is again rendered colourless by addition of an excess of trichloroacetic acid.

Afterwards the solutions required were always prepared by double decomposition of the pure barium-salt of trichloroacetic acid with ferric sulphate. The pure acid, twice distilled in vacuum (b.p. 94°,8 under 12 m.m. pressure) was converted by means of baryiumhydroxide into the barium-salt, which crystallises with varying quantities of water. A preparation with 25,3 % of Ba was precipitated with a ferric sulphate of 22,5 % of Fe and the solution was filtered several times in the cold. It has a pale yellow colour and gives no precipitate either with $BaCl_2$ or H_2SO_4; it is, moreover, not sensitive to light, but can be brought in such condition by means of an excess of trichloroacetic acid.

Another time it was tried to obtain a solution of the salt as concentrated as possible. A solution of the barium-salt containing 4 mols. pro litre, was mixed with a solution of ferric sulphate containing 1.33 mol. pro litre. The $BaSO_4$ now separates in a colloidal, very viscous mass, which prevents a complete decomposition from taking place, even when one of the solutions is poured in a thin stream and with constant stirring into the other. The filtered liquid is always rich in Ba-salt, whereas the brownish precipitate, on washing with water, yields a reddish-brown solution, which contains an excess of ferric sulphate. The direct filtrate is almost colourless and very viscous; after being analysed it is treated cautiously with ferric sulphate until it gives no precipitate with $BaCl_2$ or dilute H_2SO_4. On repeating the experiment such incomplete decomposition was noticed constantly.

Although the quantity of the highly concentrated solution thus obtained, amounted only to 200 cm³, many of its properties were studied just because the phenomena observed with these very strong solutions were much more simple than with the diluted ones. A solution containing 32,33 % by weight of iron salt, corresponding to about 0,06 gram-molecule of salt in 100 grams of solution was especially employed.

§ 3. *Properties of the solution.* It has a brownish-yellow colour but gradually turns a little darker on exposure to the air; by an excess of water it turns more of a yellowish-brown, and by an excess of trichloroacetic acid it becomes colourless.

With a little H_2SO_4 it becomes nearly colourless; with dilute H_2SO_4 also, but with a very faint tinge of sea-green.

With a little HNO_3 (S.g. 1,4) it turns almost colourless; with an excess, pale yellow. With a little strong HCl it turns greenish-yellow; with an excess intensively orange-yellow.

With acetic acid it turns yellow, with alcohol yellowish-brown, with ether blood-red and after shaking repeatedly with ether all the ferric salt may be extracted. The dried ethereal solution yields on evaporation, besides a little trichloroacetic acid, a reddish brown crystalline mass which, on analysis, appears to have a varying composition and contains about 10 % of C, 56 % of Cl and 10 to 11 % of Fe. It always contains too little C for a normal ferric trichloroacetate. Undoubtedly it is a mixture of two hexatrichloroacetato-derivatives.

A freshly prepared solution gives with $Ag\,NO_3$ a scarcely perceptible $Ag\,Cl$-reaction; old solutions yield more $Ag\,Cl$. Indeed, the same phenomenon is also found with strong solutions of the acid itself; it is based, as we shall see, on an oxydation by atmospheric oxygen.

The solution exhibits all the reactions of the ferric-ion; with potassium thiocyanate a red, with potassium ferrocyanide a blue colouration; with NH_4OH and alkali-hydroxides a precipitate of colloidal Fe_2O_3; with H_2S a separation of sulphur; with JK a liberation of iodine; with Na_2HPO_4 a white precipitate soluble in excess of trichloroacetic acid; with $(NH_4)_2S$ a black precipitate of FeS. The solution has an acid reaction. The analysis shows that the relation of $Fe : Cl$ in the solution is exactly 2 atoms of Fe to 9 atoms of Cl. There is no doubt that the behaviour is that of a solution of a true ferric salt.
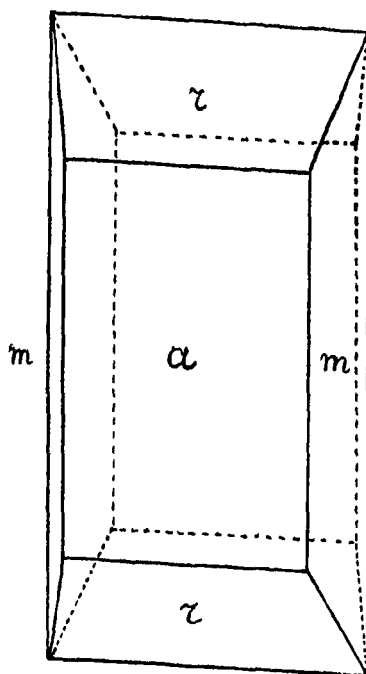

Fig. 1.

§ 4. *Behaviour in the light.* The concentrated solution is soon decomposed in daylight with evolution of a colourless gas and separation of a heavy, white crystalline precipitate with a peculiar odour.

The gas, on analysis, proved to consist of *pure carbon-dioxide.* The white substance was filtered off, sharply dried and repeatedly recrystallised from ether and alcohol. On slow evaporation the crystals shown in fig. 1 were formed. They are *rhombic-bipyramidal* as could be proved also by etching figures.

Axial relation: $a : b : c = 1,7992 : 1 : 3,1713$.

Forms: $a = \{100\}$, predominant and very lustrous; $m = \{110\}$, also yielding sharp reflexes; $r = \{101\}$ narrower and

reflecting but dully; the planes a and r are frequently striped parallel to the b-axis.

The crystals are somewhat elongated along the c-axis; they do not possess a decided cleavability.

Angular values:	Measured:	Calculated:	according to G.:	according to B.:
$a : m = (100) : (110) =$ * 60° 56′	—	60° 54′	61° 0′
$a : r = (100) : (101) =$ * 29 34	—	29 35	29 40
$m : m = (110) : (\overline{1}10) =$ 58 4	58° 4′	58 12	58 0
$r : r = (101) : (\overline{1}01) =$ 120 54	120 52	120 50	120 40
$m : r = (110) : (101) =$ 64 58	65 0	64 57	65 5

In convergent polarised light, the two branches of a dark hyperbola are noticed on a; the axial plane is probably parallel to {100}. Strong double refraction and everywhere normal extinction.

From these determinations it follows that the substance is nothing else but pure *hexachloroethane* C_2Cl_6, studied by Brooke[1] in 1824 and later, in 1904, by Gossner[2], who obtained his crystals from carbon disulphide. Gossner finds as optical axial plane {100}, with b as acute bisectrix; the double refraction is strong and negative, the dispersion: $\varrho < v$. Sp. gr. of the crystals: 2,091.

The measurements of Brooke and of Gossner are placed next to mine for the purpose of comparison; in those of Gossner, the b- and c-axis have been interchanged, but from his axial values — using the plan adopted here — the axial relation is readily calculated as $a : b : c = 1,7965 : 1 : 3,1649$.

This leaves no doubt that the two preparations are perfectly identical. A chlorine-determination after Liebig's method gave 89,75°/₀ Cl; calculated 89,87°/₀ Cl. On account of incomplete decomposition, Carius' method always gave too little Cl. The melting point is situated at 186° C.; the substance then begins to evaporate almost at once; so its triple-point-pressure can differ but little from one atmosphere.

§ 5. It soon became evident, that the splitting into CO_2 and C_2Cl_6 needs not to be the only reaction, unless special precautions are taken. First of all it was noticed that the same solution gave $CO_2 + C_2Cl_6$ in one vessel, whereas in other apparatus the liquid turned yellow, and free chlorine, readily detectable, was formed together with a very little *chloroform*; in the absence of an excess of free acid Fe_2O_3

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[1] Brooke, Ann. of Phil. **23**. 364. (1824).

[2] Gossner, Zeits. f. Kryst. und Miner. **38**. 151. (1904).

was also deposited. After a long search it was found that the cause of the reaction could not be traced to the different kinds of glass used, but was directly connected with the presence of free oxygen above the surface of the liquid. This prevents the separation of *hexachloroethane*, but on the other hand, causes the formation of Cl_2, HCl, and Fe_2O_3. In this and in other cases — as will be shown afterwards more in detail — it has been proved that trichloroacetic acid in aqueous solutions acts in a remarkable manner as an oxygen-carrier, and that the free acid itself is oxidised with elimination of free chlorine. Such can be proved by the catalytic oxidation of JK-solution by air if $CCl_3 \cdot CO_2H$ is present; a reaction which also takes place in the dark with measurable velocity. Further by the auto-oxidation of 2N.- and 4N.-acid solutions, if they are kept in contact with air; by the auto-oxidation of ferric-chloride-solutions, which all begin to get charged with Cl-ions etc.

These oxidation phenomena explain why, from a solution prepared from 240 grams of crystallised bariumhydroxide + 250 grams of trichloroacetic acid and decomposed with 100 grams of anhydrous ferric sulphate, after seven months, a quantity of hexachloroethane was obtained which amounted to only $42^0/_0$ of the theoretical yield. In the solution was still found, by titration, 0,118 gram-atom of chlorine as ion; besides about 25 grams of free trichloroacetic acid, which were obtained by direct extraction and then identified. The solution gave all the reactions for *ferrous*-ion besides these for the *ferric*-ion. As these reactions had taken place in three *open* bottles the cause must be attributed to the action of the air. In the study of the photochemical decomposition it is, therefore, necessary *to carefully exclude every trace of free oxygen.*

§ 6. *Light absorption.* A solution of 16 grams of ferric salt in 100 grams of the liquid exhibits in a layer of 10 cm. thickness the complete absorption of the visible violet, of the blue and of about $^1/_3$ of the green in the visible spectrum. If then to the solution are added 16 grams of trichloroacetic acid, the now colourless solution has a much smaller absorption-power; still, with a 10 cm. thick layer, about $^2/_3$ of the visible violet also disappeared.

The solution was now placed in four troughs which were covered with glass plates as monochromatic as possible; yellow, green, red and blue [1]). As might have been expected, *no* action whatever was observed, even after several weeks, in the red and yellow troughs; on the other hand, after a short time, action occurred in the blue

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[1]) From SCHOTT & GEN, *Jena.*

and somewhat later also in the green troughs. The decomposition in the blue light proceeded about 3 or 4 times more rapidly than in the green one.

A similar solution was placed in tubes and troughs constructed of uviol glass, and the light of three uviol lamps was concentrated thereupon by means of a uviol lens of 120 mm. diameter. After 8 hours' exposure a measurable quantity of C_2Cl_6 had already deposited. Quantitative experiments in a small uviol thermostat and also in a quartz apparatus with the aid of a quartz lamp are now being carried out; they prove anyhow, that the decomposition-velocity depends distinctly on the concentration of the solutions. Generally, the action of the ultraviolet light is again a particularly strong one.

§ 7. Further decompositions are caused by the electric current and by an elevation of temperature. The latter first causes a brown colouration owing to increased hydrolysis; afterwards evolution of CO_2 and a turbidity due to a deposit of Fe_2O_3, and liberation of *chloroform*. Quite analogous, for instance, is, as I noticed, the decomposition of a solution of *thallous-tribromoacetate* into CO_2 and $CHBr_3$ when heated at 70°, and the *photochemical transformation* of a solution of *ferric-tribromoacetate*, which always yields CO_2, Fe_2O_3 and *bromoform*.

The electrolysis of the ferric salt shows nothing much in particular. The specific resistance of the solutions is great and at first they always turn brown. At an increased current-density, an evolution of gas takes place at the anode and this gas is nothing else but *free chlorine*. Simultaneously we can observe at the cathode the formation of a ferrous salt, also the presence of much HCl which causes the resistance to gradually decrease. Hence, both the thermic and the electrolytic decompositions of the ferric salt are different from the photochemical one.

In regard to the above stated comparisons between the three transformation-forms of the ferric solutions, one might also imagine that it was practically a question of a photochemical splitting of trichloroacetic acid, in which the Fe-ion would exercise its wellknown *photocatalytic* action. It is, therefore, obvious to also compare this splitting of the $CCl_3 . CO'_2$-complex with the thermochemical and its electrolytic decomposition.

The thermochemical decomposition has been thoroughly studied; CO_2 and $CHCl_3$ are always the main products in the desintegration of the trichloroacetic acid molecule. This happens, for instance, on boiling the solution of the alkali, barium, thallous and of the ferric

24

salts. This form of decomposition is therefore, quite distinct from the photochemical splitting. The question is what the electrolysis of the acid might be able to teach us?

§ 8. In the study of the photochemical decomposition of the ferric salt of trichloroacetic acid we found $C_2 Cl_6$ and CO_2 as the main products. This splitting of the acid is apparently quite analogous to that observed in the electrolysis of the carboxylic acids and their salts [1]. KOLBE found that the acetates, in favourable circumstances, give mainly $C_2 H_6$ and CO_2; KAUFLER and HERZOG, however, get with monochloroacetic acid different results, namely, always a liberation of Cl and formation of formaldehyde; HERZOG (Diss.), however, also found in addition methylene-chloride (in the case of bromoacetic acid, methylene-bromide and with iodoacetic acid, methylene-iodide and also iodine); CRUM BROWN and WALKER obtained from ethylpotassium-malonate the diethyl-ester of succinic acid; also from succinic acid, adipic acid; from adipic acid, sebacic acid and from the latter suberic acid. KAUFLER and HERZOG succeeded, moreover, in proving, by means of an anode charged with iodine, that the formation of $C_2 H_6$ from acetic acid does not take place according to the mechanism suggested by KÉKULÉ and BOURGEOIN (Ann. d. Chem. 131 79. (1864) and Ann. de chim. phys. (4), 14. 157 (1868) neither in the manner represented by SCHALL (Z. für Electrochem. 3. 86. (1896)), but simply according to:

$$2\,CH_3 . \overline{CO} . O + 2 \oplus \rightarrow 2\,CH_3 . CO . O = 2\,CO_2 + 2\,CH_3 = 2\,CO_2 + C_2 H_6.$$
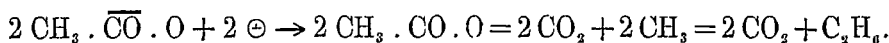
The intermediary formation of the CH_3-groups was proved by the generation of $CH_3 J$, which was fixed as phenyldimethylammonium iodide and determined as such.

Hence, if, in the electrolysis of trichloroacetic acid, $C_2 Cl_6$ could indeed be obtained besides CO_2, the photochemical splitting of the iron salt would be quite analogous to an *electrolytic* process.

This fact is of great theoretical significance. With our very imperfect knowledge of the mechanism of the photochemical reactions several theories as to its nature have originated which each have their pro and contra, according to the particular cases in which they are applied.

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[1] KOLBE, Lieb. Ann. 69. 257 (1849); JAHN. Wied. Ann. 37. 408. (1880); CRUM BROWN and WALKER, Lieb. Ann. 261. 107. (1890): KAUFLER and HERZOG, Berl. Ber. 42. 3858. (1909); FEIST, Berl. Ber. 33. 2094. (1900; VON MILLER and HOFER, Berl. Ber. 28. 2427 (1895); ELBS and KRATZ, Journ. f. prakt. Chemie, N. F. 55. 502. (1897); ELBS. ibid. (2). 47. 104; C. HERZOG, Inaug. Diss. Zürich, 1909; TROEGER and EWERS, J. f. prakt. Chem. (2). 58. 127. (1898).

For a number of years the opinion has gained ground in different quarters, that the photochemical reaction would be quite analogous to the thermochemical one at a much higher temperature of the system; that, therefore, the light chiefly increases in a high degree the "temperature" in the system of the reacting substances, which would explain the great reaction-velocity and the small temperature-coefficient thereof, etc.

Opposed to this view in a certain sense is another theory, lately defended especially by BANCROFT, in which the great analogy between the photochemical reaction and the processes, occurring in the electrolysis at the cathode or the anode is pointed out. In particular, the analogy with cathodic reductions occupies the first place. It cannot be denied that the comparison is, in many cases, strikingly correct. The decomposition-form of ferric-trichloroacetate might serve in a certain sense as an argument in favour of this theory, if the electrolysis of the acid actually proceeded in the sense of KOLBE's synthesis.

The following may serve to prove also the incorrectness of this presumption.

§ 9. If a dilute ($N/_{10}$) aqueous solution of trichloroacetic acid is electrolysed between platinum electrodes, a current of about 0,05 amp. and 5 volts being used, the only result is an evolution of O_2 at the anode and double the volume of H_2 at the cathode. Yet, a little Cl_2 may be detected towards the end at the anode besides some Cl'-ions in the liquid itself [1].

Afterwards a $N/_5$ solution was taken and submitted to electrolysis, a current of 0,17 amp. and 8 volts being used. At the commencement most of the gas is being evolved at the negative pole; the potential, however, slowly falls to 7,6 volts and after an hour the proportion between the volumes of the two gases has undergone but little modification. After four hours, however, both volumes have become equal; at the anode the evolution of the gas becomes more and more rapid whilst at the cathode a more and more retarded evolution takes place. The liquid itself gets rich in Cl'-ions, owing to which the resistance gets less and the intensity of the current a little greater. After another $3^1/_2$ hours, the volume of gas at the positive pole is already much larger than that at the negative one, and con-

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[1] This fact has always escaped notice in experiments on the determination of the electrolytic dissociation constant of trichloroacetic acid. It is very much the question, whether the well-known extraordinarily large value of K for this acid, as deduced from OSTWALD's experiments, is not to be attributed in part, to the presence of HCl in the solutions.

24*

tains chlorine to a large extent. The potential fluctuates, with shocks, between 7 and 7.4 volts.

Next a 0.68 N.-solution was taken and electrolysed with 0.3 amp. and 7.75 volts; the matter is now quite different and the same as that observed in the electrolysis of a 2 N.-solution with 0.46 amp. and 7.6 volts. In this latter case were formed *immediately*, at the positive pole, large gas-bubbles, which ascend *by fits and starts*, while a continuously and slowly ascending stream of small gas bubbles is noticed at the cathode. At the same time is formed at the liquid-meniscus above the anode a turbid looking drop, which, gradually increasing in size, detaches from the meniscus and falls down on account of its much greater density. Later, it was found that an 8 N solution of the acid gives Cl_2, CO_2, $COCl_2$, and H_2 and O_2, but no *liquid* product.

After 50 minutes the volume of the gas at its negative pole had increased to 15 cc, that at the anode, however, to 88,3 cc. The anodic gas was practically colourless and contained Cl_2, CO_2, and CO but also to a very large extent *phosgene* $COCl_2$ as was proved by its various properties and by comparison with phosgene-gas, expressly prepared for this purpose from CCl_4 and fuming sulphuric acid.

In order to have a survey as to the relative velocity of the evolution of gas at both poles, a few observations taken from one series of experiments are communicated in the table below:

Time : (in minutes)	Anodic gas-volume : (in c.c.)	Cathodic gas-volume : (in c.c.)
2	2.5	7
6	9	9
13	20	10
19	33	10.5
26	52.5	10.8
31	69.5	11,0

We notice that after a given time the evolution of hydrogen at the cathode almost ceases. Probably the hydrogen is used up for a reduction and as the whole of the liquid present in the U-tube is strongly charged with phosgene and chlorine and a considerable quantity of HCl is also formed therein, it is very probable that this H_2 is absorbed to form HCl. In these experiments the potential fell continuously until the end value of 7.25 Volts was reached.

The analysis of the anodic gas showed that its composition is not constant, particularly as regards the chlorine-content. For instance, of the 88.3 c.c. mentioned above only 6,7 c.c. consisted of Cl_2; the remainder consisted of $COCl_2$ and CO_2 with a little free O_2 and CO.

The heavy, turbid liquid was collected; on being washed with water it generally at once *solidifies*. Yet, it seems as if the product is not always the same in all conditions of temperature; for instance, the mass resulting at $0°$ remained permanently liquid under water whereas the product prepared, as usual, at $22°$ generally solidified suddenly like a strongly undercooled melt. This product, however, has always the horrible odour which reminds at once of chloral and phosgene, and experimenting with this substance consequently becomes a veritable torment.

It is decomposed by water; after some time it disappears in the liquid of the electrolyte. In that decomposition it yields volumes of phosgene. The melting point of the substance, after repeated pressing, when determined in a capillary tube, was $32°$—$34°$. With water, it yields $COCl_2$, trichloroacetic acid and Cl-ions. Hence, when heated with KOH and aniline it gives the carbylamine-reaction, thus proving the presence of $CHCl_3$ which has formed from the CCl_3COOH on boiling with potassiumhydroxide.

Analysis. The substance was prepared by electrolysis of a 27.7% trichloroacetic acid solution, a current of 1,19 amp. and 17 volts at $22°.5$ being used. It deserves notice that the liquid formed in the electrolyte has always a somewhat lower temperature than the surroundings. The substance was pressed many times and then dried in a vacuum desiccator; 0.943 gram of the substance lost 0,3706 gr. in weight thereby.

The residual mass was then analysed in duplicate according to Carius. Found $75,62\%$—75.59% average $75,61\%$ of Cl.

The compound is, therefore, nothing else but *trichloroacetic-trichloro-methyl-ester*: $CCl_3 . CO_2 . CCl_3$, — which requires $75,8\%$ of Cl.

This substance, I noticed, was indeed obtained by Elbs and Kraatz as electrolysis-product from the solution of the Na-, and Zn-salts of trichloroacetic acid. They, however, could *not* analyse it as it was always obtained by them contaminated with water and *consequently* in a continuous state of decomposition. For this ester is decomposed even by traces of water according to the equation:

$$CCl_3 . CO . OCCl_3 + H_2O = CCl_3 . CO . OH + HCl + COCl_2,$$
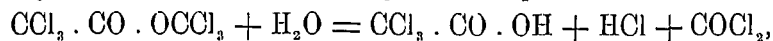
which also fully explains the formation of $COCl_2$ at the anode and that of HCl in the liquid. The melting point is given as $34°$, therefore

quite analogous to my own determination. The fact however, that the ester is formed principally at the *surface* of the liquid, also if a 4 N.-solution of the *Ba*-salt is electrolysed, seems to indicate, that the $COCl_2$ plays some role in its formation. Perhaps:

$$CCl_3 . CO . O' + HCl + COCl_2 \rightleftarrows H_2O + CCl_3 . COOCCl_3 ?$$
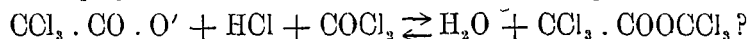
As this substance has always been previously described as a liquid, we must assume that it remains readily in the condition of an under-cooled melt; this also in connection with the low melting-point and the depression thereof caused by the H_2O and the decomposition products [1]. Indeed afterwards I found, that the pure ester, prepared by chlorination of trichloroacetic-methylester in the sunlight, remains liquid in a closed, evacuated vessel for several months!

In dry ether it dissolves readily; in alcohol or moist ether with violent evolution of gas. With NH_3 it forms a white crystalline substance of a comparatively high melting-point, which appears to be trichloroacetamide.

I also wish to observe that catalysts such as Al_2Cl_6, for instance, readily split the ester into $C_2Cl_6 + CO_2$. It would not be a matter of surprise, if also the catalytic action of the light could do this. In that case the photochemical decomposition of the ferric salt, the formation therein of CO_2, C_2Cl_6, HCl, and free $CCl_3 . COOH$, might be explained by assuming an intermediary formation of this substance; we should then have a complete analogy of the photochemical reaction with an electrolytic process. If, however, this should not be the case, — and up to the present, everything points to this, — the form of the said photochemical reaction does not seem to tally either with the one or the other of the two theoretical views.

§ 10. The fact that this singular compound is given in Beilstein's [2] manual as being identical with the *pentachloroethyl-ester of chloro-formic acid* induced me to more carefully study both substances. During this investigation I came across a short treatise of Anschütz and Emery [3], which authors had already prepared both compounds in 1893 for exactly the same purpose. Although my results agree

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[1] It should be observed that the formation of a compound: $CCl_3 . CO . OCCl_3$ in the electrolysis of trichloroacetic acid is in complete accord with the experiences of C. Herzog (Diss. Zürich 1909), who observed with monochloro-, monobromo- and dichloroacetic acid the formation of the analogously constituted esters during the electrolysis of the sodium salts.

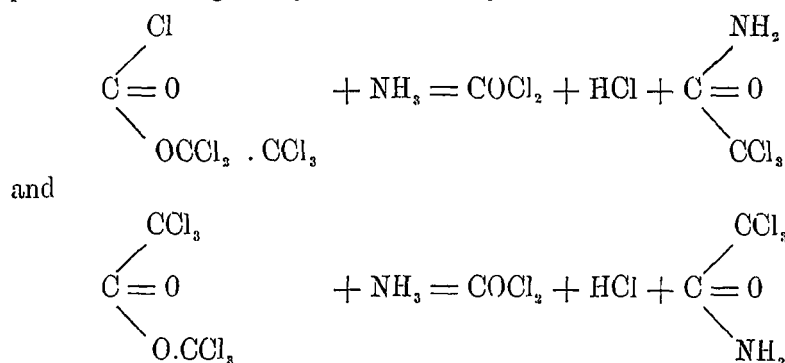[2] Beilstein's Manual, Vol. I. 471. (1893); corrected in Suppl. Vol. I. p. 167. (1901).

[3] Anschütz and Emery, Ann. der Chem. 273. 56. (1892).

with theirs, a few particulars of the research may be communicated here because, at the end of their treatise, they seem to want further confirmations of their *data* which are opposed to those of H. Mül-ler[1]. Moreover, a few additional *data* may be mentioned here.

The idea that $CCl_3 . CO_2 . CCl_3$ and $Cl . CO . O . C_2Cl_5$ should be identical is derived from Cloëz[2]. He bases his view chiefly on the fact that both esters lead, with H_2O, NH_4OH, alkalis, alcohol etc. to *the same* end-products.

Like $CCl_3 . CO . OCCl_3$, the compound $Cl . CO . OC_2Cl_5$ is also converted by water into trichloroacetic acid, carbon-dioxide and hydrogen-chloride; the phosgene formed at first is decomposed by water into CO_2 and $2 HCl$.

The reaction with NH_3, which in both cases leads to trichloro-acetamide, also seems to prove such. It is, however, plain that by accepting, — according to Cloëz, — the splitting off of $COCl_2$ as the first reaction-stadium, we can obtain from both esters the same products, although they are differently constituted.

$$\begin{array}{c} Cl \\ / \\ C = 0 \\ \backslash \\ OCCl_2 . CCl_3 \end{array} + NH_3 = COCl_2 + HCl + \begin{array}{c} NH_2 \\ / \\ C = 0 \\ \backslash \\ CCl_3 \end{array}$$

and

$$\begin{array}{c} CCl_3 \\ / \\ C = 0 \\ \backslash \\ O.CCl_3 \end{array} + NH_3 = COCl_2 + HCl + \begin{array}{c} CCl_3 \\ / \\ C = 0 \\ \backslash \\ NH_2 \end{array}$$

and something similar applies also to the other reactions he has given.

If therefore, Cloëz's arguments cannot at all be considered as final, they may now, after the experiments of the German authors and those of myself, be considered as totally unsatisfactory.

Pure, repeatedly distilled chloro-formic ethyl-ester was, with exclusion of all moisture, chlorinated in bright sunlight[3]. From the yellow, very heavy liquid the chlorine is expelled by CO_2 and the product distilled under reduced pressure. As the main fraction was obtained a colourless liquid having the same odour as $CCl_3 . CO . OCCl_3$, which boiled at 129° under 80 mm. pressure, at 116° under 50 mm. pressure and at 104° under 22 mm. pressure. After fractionating

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[1] Müller, Ann. der Chemie. 258. 61. (1890).

[2] Cloëz, Ann. de Chim. et phys. (3). 17. 300 (1846).

[3] In these experiments I have been zealously supported by my assistant Mr. J. B. Menke, to whom I again bring my best thanks.

twice, the ester appeared to boil without decomposition at 205°,2 under 758 mm. pressure. The solidifying point was constant at 23°,7. The compound, like the trichloroacetic-trichloromethyl ester, has a strong tendency to undercooling; after inoculation it crystallises immediately, but with little linear velocity. The heat of crystallisation is rather considerable. The sp.gr. at 23°,5 was 1,7336.

From the melt, the substance crystallises in thin, colourless, monoclinic plates or needles with rectangular limitations. They are frequently blunted at the angles and show right extinction. The crystals exhibit a strong double-refraction; the smallest elasticity-axis coincides with the longitudinal direction, which direction is also that of the optical axial plane. In convergent light an optical axis is visible at the border of the field of view; the bisetrix is of a negative character, while the dispersion is exceedingly feeble so that it could not be ascertained for what wave-length the axial angle is the largest.
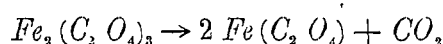
With NH_4OH it gives trichloroacetamide with strong evolution of heat. It *differs* from $CCl_3 . CO . O . CCl_3$ although the esters are so analogous that they may almost be mistaken for each other. The penetrating odour of phosgene and chloral, which both esters possess, is however much more pronounced with the $CCl_3 . CO . OCCl_3$ than with the pentachloro-derivative, a fact, which is no doubt directly connected with the other point of difference, viz. that $ClCO_2C_2Cl_5$ is evidently decomposed by cold water much more slowly than the trichloroacetic acid derivative. Moreover their melting points differ more than 10°. According to ANSCHÜTZ and EMERY the substance obtained by chlorination of trichloroacetic-methyl-ester boils at 96° under 22 mm. pressure; the pentachloro-derivative obtained by myself at 104°.

The difference between the two substances, therefore, admits of no doubt; a quantitative comparison as to their reaction-velocities is in progress.
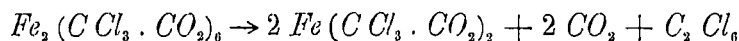

§ 11. As regards the mechanism of the studied photochemical decomposition it has been shown, by the experiments made up to the present, that the decomposing substance can be considered as the normal ferric-trichloroacetate: $(C Cl_3 CO . O)_3 Fe.$

With very concentrated solutions contained in uviol-glass tubes, a separation of $C_2 Cl_6$ takes already place after eight hours' exposure to the light; with dilute and consequently brown-coloured solutions a little trichloro-acetic acid should be added first for the purpose of decolourisation, that is to say for modification of the light absorption. Still it is doubtful whether that addition really accelerates the process; from the data at disposal I should feel more inclined to conclude
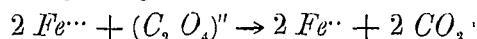
to a retarding action; which might then perhaps be explained in that sense, that it is really the $(CCl_3CO . O')$-ion, previously combined with the $Fe^{...}$-ion in some very definite manner, and split off from this, which is resolved. All this is still problematical. One should rather feel inclined to put this photochemical reaction quite on a level with that of ferric oxalate:
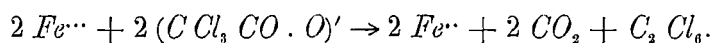
$$Fe_2(C_2 O_4)_3 \rightarrow 2 Fe(C_2 O_4) + CO_2$$

and:

$$Fe_2(C Cl_3 . CO_2)_6 \rightarrow 2 Fe(C Cl_3 . CO_2)_2 + 2 CO_2 + C_2 Cl_6$$

or if we assume a splitting of ions;

$$2 Fe^{...} + (C_2 O_4)'' \rightarrow 2 Fe^{..} + 2 CO_2 \cdot$$

and:

$$2 Fe^{...} + 2 (C Cl_3 CO . O)' \rightarrow 2 Fe^{..} + 2 CO_2 + C_2 Cl_6.$$
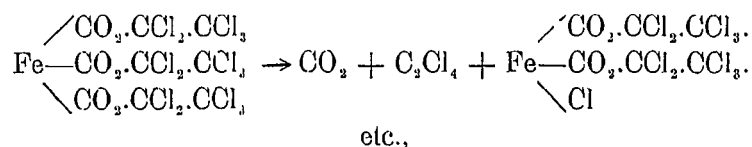
It is, however, still the question whether this conclusion is fully justified and whether it is not probable that several more intermediary stages occur; this will have to be elucidated by further research.

§ 12. Finally we may mention a few experiments with solutions of *ferric-pentachloropropionate*, of which a sensitiveness to light was fully to be expected on account of the experience, gained during this investigation.

The acid for this purpose was handed over to me by my colleague BOËSEKEN to whom I again bring my thanks. The melting-point is situated between 210° and 215°; the chlorine-content, according to B.'s statement has been found as 72.05%—71.78%; theory : 72%.

The preparation of the Ba-salt by neutralisation at the temperature of the room, presented difficulties in so far that a sweet smelling oil separated even in the dark. Nevertheless, the neutralised solution was precipitated with the calculated quantity of ferric sulphate and by repeatedly filtering in the dark and in the cold a clear greenish-yellow solution was obtained. This is very sensitive to light and gets very soon decomposed into CO_2 and a heavy colourless oil with formation of large quantities of Cl'-ion in the solution. The oil was separated, purified and dried and identified as C_2Cl_4. The photochemical splitting of ferric-pentachloropropionate is therefore perhaps represented by:

$$\text{Fe}\begin{matrix} \diagup CO_2.CCl_2.CCl_3 \\ -CO_2.CCl_2.CCl_3 \\ \diagdown CO_2.CCl_2.CCl_3 \end{matrix} \rightarrow CO_2 + C_2Cl_4 + \text{Fe}\begin{matrix} \diagup CO_2.CCl_2.CCl_3. \\ -CO_2.CCl_2.CCl_3. \\ \diagdown Cl \end{matrix}$$

etc.,

until, probably, $FeCl_3$ alone finally remains; the colour of the liquid is brownish yellow.

From this it appears that this photochemical transformation is quite analogous to that which the acid itself, according to BoÖsEKEN, undergoes by *heat*. From what has been stated above, this reaction cannot be put on a level with the photochemical decomposition of the trichloroacetate, without further evidence.

15 September 1911.

Labor. for Inorg. and Phys. Chem.
of the Univ., Groningen.

Chemistry. — "*A remarkable case of isopolymorphism with salts of the alkali-metals*". By Prof. F. M. JAEGER. (Communicated by Prof. P. VAN ROMBURGH.)

(Communicated in the meeting of Sept. 30, 1911).

§ 1. The numerous researches which have been made to explain the morphotropic relation of the alkali-metals, may be said to have led to no other view but the conviction, that the problem of the mutual replacement of these metallic atoms is one of an almost hopeless complexity.

The most accurate researches in this dominion, — those of TUTTON, — lead the author, with complete negation of all other well established facts, to the conclusion that anyhow the metals K, Rb and Cs possess plainly an isomorphotropic relation, which numerically runs parallel with the rise of their atomic weights, and that (NH_4) and Tl are, in many respects, to be placed outside the series; but that with an eventual form relation the (NH_4)-radical exerts an influence which stands between that of Rb and Cs. As to the optical properties, no regularities seem to occur. As is well known, TUTTON's beautiful researches only relate to the alkali-sulphates, the alkali-selenates and the monoclinic double sulphates and double selenates of the formula : $R'_2 Me'' (SO_4)_2$, $6H_2 O$ and $R'_2 Me'' (Se O_4)_2$, $6H_2 O$.

Even in these researches it seems here and there, that the conclusions drawn must be considered as being *too* general. For instance, with the selenates, the Tl-compound is very analogous to the Rb-salt ; the difference in molecular volume is here only $0,4^o/_0$, as against $1,4^o/_0$ between the Rb- and (NH_4)-salt. With the sulphates this difference between the Rb- and Tl-salt is about $0,8^o/_0$, between Tl- and (NH_4)-salt only $0,08^o/_0$, and a similar trifling difference between (NH_4)- and Tl-salt is also observed with ammonium-zinc-sulphate and thallous-zinc-sulphate $(0,03^o/_0)$, so that the place of