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introduced into the literature the expression *Emissarium* or *outlet of water*, which more clearly indicates the notion than the word *"Hydathode or water way"*.

It is thus evident from the second part of this communication on the secretion of water in the plant, that a secretion of liquid not only takes place in the leaves, but often also in the floral region and on various parts of the flower.

These observations place in a different light the well-known phenomenon of water-secretion in the flower-bud of plants with so-called water-calyces

Formerly we considered, that the secretion of water in the flower-bud was to be regarded as a useful arrangement, arisen in the struggle for life by natural selection, in order to protect the enclosed parts of the flower against dessication.

We now see that it is related to the phenomenon of the secretion of liquid on the surface of the plant and that the presence of water in the calyx is to be explained thus, that the water secreted by the glands of calyx and corolla is less exposed to evaporation in the closed calyx and so can collect there.

In other words, the secretion of water in the flower-bud did not arise because it is useful to the plant, but it may nevertheless be of advantage to the plant in these cases where the enclosed parts of the flower or the young fruits are exposed to the danger of dessication.


Chemistry. — *"Contribution to the knowledge of catalytic phenomena"*. By Prof. J. Boeseken. (Communicated by Prof. A. F. Holleman).

(Communicated in the meeting of October 30, 1909).

I.

Through the researches of Perrier (Thesis 1896 and Comt. rend. **116**, p. 1300) and of myself (Rec. 1900, p. 19) it has been shown that in the reaction of Friedel and Crafts it is not the aromatic hydrocarbon but the chloride or the anhydride which is attacked first by the aluminium chloride, as in many cases additive products could be isolated. These are then converted by the benzene derivative. Afterwards I have pointed out (Proc. 1907, p. 613), that the formation of these intermediate products cannot, as such, serve to explain the

catalytic influence of aluminium chloride, because the potential fall of the reaction:

$$R . Cl + Al Cl_3 = RCl . AlCl_3 \cdot$$
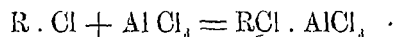
must necessarily be deducted from the potential fall of the entire reaction, so that one must still search for the cause of the velocity of these intermediate reactions.

The chlorides which form these additive products with difficulty, or not at all, such as $C Cl_4$, $CH Cl_3$, $S_2 Cl_2$, $P Cl_3$ etc. are as a rule attacked with greater violence than those which form solid molecular compounds with the catalyst.

As a matter of fact, I have come to the conclusion, and have stated so previously on account of the conversion of yellow phosphorus into the red modification (l. c.) that the explanation of the catalytic action must be looked for in the dissociating influence which the catalyst exercises when nearing the molecules.

Whatever we may think of the cause of the permanent coherence of the molecules, it is certain that there exists between the atoms a certain contrast, which cannot be quite effaced because the atoms cannot annihilate each other.

This contrast appears to be dependent on circumstances; if these change, the contrast also changes and this causes a modification in the existing equilibrium. To these changes belongs the approach of other atoms or atom-groups. The action of positive catalysts may now be represented as being that of atoms or atom-groups which owing to their immediate proximity so modify the existing contrast that another equilibrium can be attained by the first molecule.

In the reaction of FRIEDEL and CRAFTS, I therefore, assume that in the first place the aluminium chloride loosens the cloride (perhaps also the double bonds in the benzine derivative, for it appears that $AlCl_3$ exercises a condensing influence on unsaturated solutions, the least on benzene itself as was to be expected), and that the reaction can then take its course in the usual manner.

There are in the literature many indications that aluminium chloride has a purily dissociating action: I will mention the following cases. Methyl (ethyl) perchloroformate is resolved into CO_2 and CCl_4 (C_2Cl_6) (HENTSCHEL J. pract. [2] 36 p. 100 and MÜLLER Ann. 258 p. 61), Pentachloroethane is decomposed into HCl and C_2Cl_4 MOUNEYRAT Bull. [3] 19 p. 179), $CH_2Cl . CH_2Cl$ into HCl and C_2H_3 (Bull. [3] 19 p. 445), Propyl chloride yields HCl and propylene (MOUNEYRAT Bull. [3] 21 p. 616) etc.

Sulphurylchloride is resolved into SO_2 and Cl_2 (RUFF Ber. 1902

p. 4453), Oxalyl chloride, on heating gently, into CO and COCl$_2$ (H. Staudinger Ber. 1909 p. 3566).

In order to test the above view more closely I have added to these examples a few others, my chief object being to demonstrate (so as to elucidate the action of the catalyst in the Friedel and Craft's reaction) that, in the first place the chlorine atom is loosened. As a rule the chlorine atoms will leave the molecule as such in a few instances only; this may be demonstrated, for instance, by gently warming C$_2$Cl$_6$ with aluminium chloride and it is this cleavage which causes no doubt the very complex course of the reaction between perchloroethane and benzene.

Considering that the reaction might proceed more readily if during the decomposition stable chlorine compounds such as HCl could be formed, I have chosen the following four substances: trimethylacetyl chloride, dichloroacetylchloride, chloral and trichloroacetyl chloride, which all contain the more or less overloaded CO-group, so that the reaction could be watched by the evolution of the carbon monoxide.

It is certainly remarkable that, notwithstanding the excess of chlorine atoms, trichloroacetyl chloride is the most difficult to attack. A priori, there is not much to say as to the velocity of these reactions. The result of this research seems to point out that the reaction proceeds particularly smoothly in the case where H and Cl atoms are present next to two adjacent C atoms and that in the second place the overloading plays a role.

Of the three other substances the trimethylacetyl chloride is the one attacked most readily, whereas the two isomers dichloroacetyl chloride and chloral do not show large differences.

In all cases, however, the reaction takes place in such a manner that the movable Cl atom combines either with an H atom or a molecule residue, in which case a molecule of carbon monoxide is always evolved.

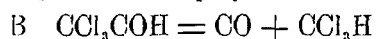I. Trimethylacetyl chloride is resolved at 0° according to the equation:

$$(CH_3)_3CCOCl = HCl + CO + C_4H_8$$
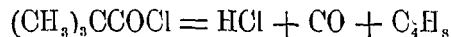
the isobutene is nearly entirely polymerised.

II. Chloral on being heated gently is decomposed in two directions.

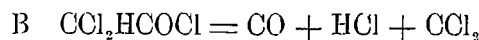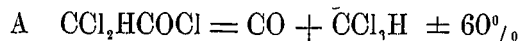$$A \quad CCl_3COH = HCl + CO + CCl_2 \pm 70-75°/_0$$
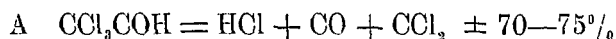
and the CCl$_2$ residue is polymerised to C$_2$Cl$_4$

$$B \quad CCl_3COH = CO + CCl_3H$$

a slight resinification cannot be entirely prevented.

III. Dichloroacetyl chloride, on being heated gently, is also decomposed in two directions.

$$A \quad CCl_2HCOCl = CO + CCl_2H \pm 60^0/_0$$

$$B \quad CCl_2HCOCl = CO + HCl + CCl_2$$

the latter being presumably polymerised to C_5Cl_{10}.

IV. Trichloroacetyl chloride, when distilled repeatedly with $AlCl_3$ is decomposed in one direction:

$$CCl_3COCl = CCl_4 + CO$$
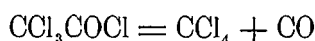
The first part of the research, a contribution to the theory of the decomposing action of aluminium chloride was herewith attained.

II.

As regards our second object, namely, the finding of the point attacked in the decomposition, the different behaviour of chloral and dichloroacethyl chloride gives already some indications.

If we assume that one of the Cl-atoms of the chloral is detached we may expect it to combine with the movable H-atom to form HCl and this indeed takes place. If the CO group or the H-atom were the point attacked we ought to obtain chloroform which I have now been able to isolate in very small quantities only.

On the other hand, and for the same reason, the formation of chloroform from dichloroacethyl chloride is to be expected; it is now the movable chlorine atom which is detached first; CO and CCl_2H then follow immediately. Being the most unsaturated one the latter group will combine with the chlorine atom to chloroform, hydrogen chloride occurring as by-product. The actual course of the reaction is therefore quite in harmony with the assumption that primarily the movable chlorine atom is rendered active.

The action of aluminium chloride on trimethylacetyl chloride is too violent to decide anything as to the first stadium of the reaction.

[That the chlorine atom exercises again a preponderating influence on the instability of the molecule is shown from the behaviour of the otherwise quite analogous pinacolin; this simply unites with the catalyst without forming a trace of CO even at 100°].

I have, therefore, observed the action of concentrated H_2SO_4 in regard to trimethylacetyl chloride because the behaviour of this acid is in many cases analogous to that of $AlCl_3$ and also because it forms the same kind of additive products (Recueil 1905, p. 222).

In this investigation the reaction appeared to pass through the following phases :

I $(CH_3)_3 C.COCl + H_2SO_4 = (CH_3)_3 C.COSO_4H + HCl$

II $(CH_3)_3 CCOSO_4H = H_2SO_4 + CO + C_4H_8$
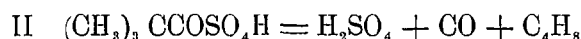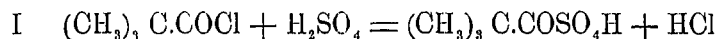
in which the isobutene was again first polymerised and then dissolved on prolonged action of the acid, with formation of sulphonic acids (BISTRYCKI and MAURON Berichte **40** p. 4377) and sulphur dioxide.

The chlorine atom is, therefore, first detached by the H_2SO_4 and in an analogous manner we may expect the same from $AlCl_3$.

Sulphuric acid itself supplies an H-atom; on using $AlCl_3$ this hydrogen must be withdrawn from the acid-chloride so that the two phases noticed separately when sulphuric acid was employed as catalyst, coincide in this case.

[It may be pointed out here that a 20% "Oleum" acts almost as energetically as $AlCl_3$. It is very probable that the real catalyst in sulphuric acid is the SO_3 which in concentrated acid is not utterly paralysed by the H_2O present].

Although the expulsion of the chlorine could be shown in a single (see above) instance only, I think I have succeeded in demonstrating from the progressive change of the reactions and also by indirect means, that the chlorine atom is rendered more movable.

In the reaction of FRIEDEL and CRAFTS we must imagine that besides the chloride, the benzene derivative, being an unsaturated compound, is also rendered active by aluminium chloride which undoubtedly will take place most readily when the chloride, catalyst and benzene derivative form one homogeneous phase. The significance of the so-called ferments of G. GUSTAVSON (J. pr. Chem. [2] 68 p. 209—234) must be particularly looked for in the fact that these are *very* loose compounds in which the three kinds of molecules mentioned have arrived in each others, immediate proximity.

The fact that the rays of light introduce the halogens into the chain must, therefore, be explained by assuming that the double bonds of benzene are rendered less active by the chemical rays than the hydrogen atoms in the chain, whereas on the other hand the latter are not rendered quite so active by aluminium chloride.

The experimental details of this research will be published elsewhere.

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